

Material science examination on pineapple fruit puree and raw material

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Abstract

Dem Ananas (*Ananas comosus* (L.) Merr) kommt unter den kommerziellen, tropischen Früchten eine große Bedeutung zu. Normalerweise wird Ananaspüree als Sterilkonserve in Dosen oder durch als Gefrierkonserviert. Ein Frischeprodukt in Pureeform ist nicht bekannt. Allerdings treten Probleme während der Lagerung oder dem Mischen auf. Die mangelnde Stabilität führt zu einer Trennung in Fasern und Serum. Das Ziel dieser Arbeit war es, die Stabilität des Ananaspürees durch Verwendung verschiedener Hydrokolloide wie Pektin, Johannesbrotkernmehl, Guarkernmehl und Xanthan zu verbessern.

Die Ergebnisse haben gezeigt, dass die Qualität des Ananasproduktes vom Reifegrad abhängig ist. Mit zunehmendem Reifegrad wurde die Farbe des Zellstoffes dunkler und die Ananas war weicher. Im Fall des Pektin einsetzes zur Pureeherstellung wurden die Parameter Pektintyp (Zitrus und Apfel), Pektinkonzentration, Veresterungsgrad und Konzentration an zugesetzten Calciumionen betrachtet. Die Ergebnisse haben gezeigt, dass Zitruspektin eine höhere Stabilität und Viskosität aufweist als Apfelpektin. Ein hoher Veresterungsgrad resultierte in einer guten Stabilität allerdings war die resultierende Viskosität nicht sehr hoch. Die Zugabe von Calciumionen hatte den größten Effekt auf Pektin mit niedrigem Veresterungsgrad. Zusätzlich wurde für Johannesbrotkernmehl, Guarkernmehl und Xanthan der Effekt der Konzentration und der Temperatur auf die rheologischen Eigenschaften der Hydrokolloidlösungen untersucht. Die Stabilität und Viskosität des Johannesbrotkernmehls und des Guarkernmehls stieg mit steigender Konzentration. Der Temperatureffekt auf die rheologischen Eigenschaften war signifikant für höhere Hydrokolloidkonzentrationen im Fall des Johannesbrotkernmehls und Guarkernmehl. Xanthan zeigte das gleiche Verhalten bezüglich der Viskosität und Stabilität mit steigender Konzentration. Allerdings hatte die Temperatur keinen signifikanten Effekt auf die rheologischen Eigenschaften. Eine Mischung aus Johannesbrotkernmehl und Xanthan induziert einen synergistischen Effekt bezüglich der Stabilität der Hydrokolloidlösung.

Der Effekt der zugesetzten Hydrokollide auf die rheologischen Eigenschaften wie Viskosität und Stabilität des Ananaspürees wurde unter Verwendung verschiedener Hydrokolloide, sowie Hydrokolloid- und Zuckerkonzentration untersucht. Die Verwendung von amidiertem Pektin führte zu einer besseren Stabilität und Viskosität als Pektin. Zusätzlich erhöhten sich die Stabilität und Viskosität von Ananaspüree mit steigender Pektinkonzentration. Der Zusatz von Zucker zum Püree führte zu einer reduzierten Stabilität aber zu einer erhöhten Viskosität. Die Stabilität des Pürees unter Zusatz von 0,2 - 0,8 % Johannesbrotkernmehl nahm rapide ab, bis sich ein konstanter Stabilitätslevel ab einer Konzentration von 1 % einstellte. Der Temperatureffekt auf die Stabilität war signifikant für höhere Konzentrationen von Johannesbrotkernmehl. Die Stabilität von Ananaspüree nahm ab mit steigender Konzentration von Guarkernmehl. Wohingegen die Viskosität anstieg. Die Temperatur hatte einen größeren Einfluss auf die Stabilität des Pürees je höher die Konzentration des Guarkernmehls war. Die Stabilität und die Viskosität von Ananaspüree unter Zusatz von Xanthan nahmen mit steigender Konzentration zu. Die Temperatur hatte keinen signifikanten Einfluss auf Stabilität und Viskosität. Als Schlussfolgerung kann die Temperaturbeständigkeit/stabilität des Ananaspürees unter Zusatz von Xanthan als vorteilhaft gegenüber dem Zusatz anderer Hydrokolloide bewertet werden. Ein synergistischer Effekt von Xanthan und Guarkernmehl bezüglich einer besseren Stabilität und Viskosität war besser als bei der Mischung von Xanthan und Johannesbrotkernmehl.

Zusammenfassend kann Xanthan als geeigneter Stabilisator für Ananaspüree bewertet werden. Nachteilig muss allerdings der nicht ausreichende Viskositätslevel angemerkt werden. Daher muss in Bezug auf eine hohe Stabilität und Viskositätslevel dies Mischung aus Xanthan und Guarkernmehl im Verhältnis 25:75 einer 1 prozentigen Lösung favorisiert werden.

Abstract

Pineapple (*Ananas comosus* (L.) Merr.) is the one of importance commercial tropical fruit. It grows on several countries, such as Thailand, Philippines and South America. The pineapple puree is one of primary product in many industries, such as bakery industry, which uses it as fruit filling. Normally pineapple puree is preserved as pineapple puree can or pineapple puree frozen. However, pineapple puree has a problem during storage or after blending. Pineapple puree is not stable structure and will be separated into serum and fiber during storage. The aim of this work was to increase the stability of pineapple puree structure by using selected gums as stabilize. The gums used in this study such as pectin, locust bean gum, guar gum, xanthan gum.

Results have shown that the quality of pineapple fruit was depending on the level of maturity. Pineapple was softer and color of pulp was darker when level of maturity increased. The properties of gums solution were investigated before added to pineapple puree by using the rheological methods, such as shear rate examination and oscillation test. In the case of pectin, the effect of pectin type (citrus and apple pectin), pectin concentration, DE, concentration of added Ca-ion on rheological properties were investigated. Results showed that citrus pectin performed higher stability and viscosity than apple pectin. High-DE exhibited good stability, but the viscosity was not high. Ca-ion adding had the great impact on low-DE pectin. In addition, LBG, guar and xanthan gum, were studied to determine the effect of concentration and temperature on rheological properties of gums solution. Results showed that stability and viscosity of LBG and guar gum was increased with increasing the gum concentration. The temperature effect on rheological properties of LBG and guar gum was at higher gum concentration distinctive. Xanthan gum also showed the increased stability and viscosity with concentration. However, temperature didn't have impact on xanthan gum compared to LBG and guar gum. Mixture of LBG and xanthan gum indicated Synergistic effect on stability of gum solution.

The effect of adding gums in pineapple puree on rheological properties such as stability and viscosity was carried out using different gums and at different gum and sugar concentration. Application of amidated pectin resulted better stability and viscosity than normal pectin. In addition, the stability and viscosity of puree was increased with increasing of pectin concentration. Adding sugar in puree resulted decreasing the stability, but increased the viscosity of puree. The stability of pineapple puree containing LBG was decreased rapidly after adding 0.2 to 0.8 % gum concentration. After adding gum more than 1 % the stability of pineapple puree remains unchanged. Temperature effect on stability of pineapple puree containing LBG was particularly at higher gum concentration distinctive. The stability of pineapple puree containing guar gum resulted decreasing with increasing of gum concentration, but viscosity increased. The temperature has at higher concentration of gum more effect on stability of pineapple than at low gum concentration. The stability and viscosity of pineapple puree containing xanthan gum was increased with increasing of xanthan concentration. In contrast, temperature don't show any distinct effect on stability of pineapple puree containing xanthan. Thus, temperature resistance of pineapple puree supplemented with xanthan gum was better than other gum. Synergistic of xanthan and guar gum on the stability and viscosity was better than xanthan and LBG.

In conclusion, xanthan gum performed was suitable stabilizer for pineapple puree, but viscosity was insufficient. Thus, the mixture of xanthan gum and guar gum was the best choice in term of high stability and very good viscosity of pineapple puree.

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NOMENCLATURE

Latin letters

<i>a</i>	Red (+) to green (-)	-
<i>a₀</i>	Red and green color of target sample	-
<i>A*</i>	Frenkel-Eyring constant (Eq. 3.2)	Pas
<i>A</i>	Area	m ²
<i>A_T</i>	Area of Texture diagram	N-mm
<i>A_{TH}</i>	Thixotropic area	Pa/s
<i>b</i>	Yellow (+) to blue (-)	-
<i>b₀</i>	Yellow and blue color of target sample	-
<i>c</i>	Concentration	%
<i>c_{lbg}</i>	Concentration of Locust bean gum	%
<i>c_{gg}</i>	Concentration of guar gum	%
<i>c_{xg}</i>	Concentration of xanthan gum	%
<i>c_s</i>	Concentration of sugar	%
<i>COD</i>	Determination of chemical Oxygen Demand	mg/ 100 g.
<i>d_{3.2}</i>	Surface area diameter	m
<i>d_{4.3}</i>	Volume mean diameter	m
<i>d₁₀</i>	Diameter on 10 % cumulative	m
<i>d₅₀</i>	Median size diameter	m
<i>d_T</i>	Particle diameter	m
<i>DA</i>	Degree of amidation	%
<i>DE</i>	Degree of esterification	-
<i>DM</i>	Degree of methylation	%
<i>E_a</i>	Flow activate energy	Kj/mol
ΔE	Total color difference	-
<i>f</i>	Frequency	Hz
<i>F</i>	Force	N
<i>F_{max}</i>	Maximum force	N
<i>G</i>	Modulus	Pa
<i>G'</i>	Storage modulus	Pa
<i>G''</i>	Loss modulus	Pa
$ G^* $	Complex modulus	Pa
<i>K</i>	Consistency factor	Pa·s ⁿ
ΔK	Difference of consistency factor	Pa·s ⁿ
<i>L</i>	Lightness	-
<i>L₀</i>	Lightness of target sample	-
<i>M_w</i>	Weight molecular weight	Daltons
<i>M_n</i>	Number of molecular weight	Daltons

\overline{M}_w	Weight average molecular weight	Daltons
\overline{M}_n	Number average molecular weight	Daltons
N	Non-heating	-
n	Flow index	-
Δn	Difference of flow index	-
r	Correlation coefficient	-
R	Universal gas constant	kJ/mol·
t	temperature	°C
t_{20}	Temperature at 20°C	°C
t_{60}	Temperature at 60°C	°C
T	Temperature	K
T^*	Absolute temperature	K
TTS	Total soluble solid	°Brix
s	Distance	mm

Greece Letter

γ	Shear strain or deformation	-
$\dot{\gamma}$	Shear strain rate or shear rate	1/s
η	Viscosity	Pa·s
η_{eff}	Effective viscosity	Pa·s
$\eta_{eff} (50/s)$	Effective viscosity at maximum shear rate 50/s	Pa·s
$\eta_{eff} (1000/s)$	Effective viscosity at maximum shear rate 1000/s	Pa·s
η_{CA}	Casson viscosity	Pas
η_{BH}	Bingham viscosity	Pas
η_{dyn}	Dynamic viscosity	Pas
η_{proz}	Process viscosity	Pas
$\Delta\eta_{eff}$	Difference of effective viscosity	Pa·s
τ	Shear stress	Pa
τ_0	Yield point	Pa
$\tan \delta$	Loss factor	-
σ	Normal stress	Pa
Δ	Difference	-

Abbreviations

<i>AU pectin</i>	Apple pectin
<i>CU pectin</i>	Citrus pectin
<i>CMC</i>	Carboxymethyl cellulose gum
<i>CSR</i>	Control shear rate
<i>DIN Norm</i>	Deutsches Institut für Normung e.V. (DIN German standards and standardization)
<i>DG Norm.</i>	Double gap type of rheological head
<i>FDA</i>	American food and drug administration

<i>FAO</i>	Food and Agriculture Organization
<i>GG</i>	Guar gum
<i>GG/XG</i>	Guar/Xanthan gum mixture
<i>GRAS</i>	Generally recognized as safe
<i>H</i>	Heating
<i>HB</i>	Herschel Bulkley model
<i>HM-pectin</i>	High Methy ester Pectin
<i>HPMC</i>	hydroxylpropylmethylcellulose
<i>LBG</i>	Locust bean gum
<i>LBG/XG</i>	Locust bean /Xanthan gum mixture
<i>LM-pectin</i>	Low Methy ester Pectin
<i>MT</i>	Million Tons
<i>MP</i>	Maturity phase
<i>OW</i>	Ostwald-de Waele model
<i>RSM</i>	Response surface methods
<i>XG</i>	Xanthan gum

Chapter 1 Introduction

Pineapple (*Ananas comosus* (L.) Merr.), botanically is a member of the ornamental Bromeliaceae, originated in tropical South America but is widely grown in all tropical and subtropical areas of the world, such as Thailand, The Philippines, China and South America countries. Pineapple was consumed as raw and processing product, such as pineapple can, dry pineapple, pineapple puree and pineapple juice. More than 4.5×10^6 tons, both fresh and can, marketed worldwide each year. Thailand is one of world's leading producer and exporters of pineapple fruit and pineapple products. According to the most recent statistics of Food and Agriculture Organization (FAO) of United Nations (2006), sales of pineapple by Thailand to the world market were worth USD 2.6 million in 2005. Pineapple is the one of most suitable food as diet and health food, because it contains low fat, high fiber and high vitamins. Moreover, pineapple can improve the digestion system as well.

Pineapple puree is one of enrich product of pineapple. Pineapple puree is an importance primary product for producing the baby food or fruit filling in bakery products. Puree is made by using different method, such as high pressure method, osmosis extraction or normal blending. In factories, pineapple puree is packed in can or plastic bag until using. Thus, structure of puree must strong enough to retain the viscosity and properties during storage. Basically, pineapple puree was separated into two phases after blending or during storage: serum and fiber. It is necessary to improve the stability of the structure of pineapple puree. Using a stabilizer is a significant method for improving the properties of puree.

Gums are applied in pineapple puree to play a role as stabilizers. There are many kinds of gum which can be grouped by using production source. It can divide into two groups: plant gums and microbial gums. The plant gum is the gum, extracts from some part of plant. For example, pectin is extracted from the apple puree or citrus peel. Locust bean, guar and tara gum are called "seed gum", because they are extracted from seeds. The plant gum is often used in industries, because low cost and advantage viscosity. Furthermore, the process of extraction is not complicated.

A further group is microbial gum group. Gums in this group are extracted from animals. For example, xanthan gum is extracted from bacteria "*Xanthomonas campestris*". Properties of xanthan gum, such as those that enhance viscosity or stability, are better than plant gums, but the cost of production is higher than plant gums. Thus, in some product used xanthan gum and plant gum mixing in order to reduce the cost. Moreover, the plant gums, such as locust bean gum, are able to have the synergistic with xanthan gum. Consequently, the properties of gums, such as stability and viscosity, performed better than properties of single gum.

The problem and purpose for investigating this subject has been described in Chapter 1. Chapter 2 is the Aim and scope of work. Chapter 3 outlines some information concerning pineapple, gums and rheological properties. Chapter 4 describes the materials and methods, includes flow charts of overall work in this study. Chapter 5 showed result of investigation for characteristics of pineapple fruit at different level of maturity. Chapter 6 demonstrates the results of materials science investigation of gums. Chapter 7 shows the results of material science investigation for pineapple puree with gums. Chapter 8 was compared between pineapple puree production and selected commercial puree product, such as baby food and apple puree.

Chapter 2 Objective of work

The structure of pineapple puree is not stable after blending or during storage. Pineapple puree will be separated into two phases: the serum on bottom and fiber or pectin on the top of pineapple purees. Pineapple puree supplemented with gum could in order to stabilize the structure. The main objective of this study was to investigate the ability of selected gums, such as pectin, guar, locust bean and xanthan gum, to stabilize the structure of pineapple puree. The following experimental steps are carried out in this study:

1. To study characteristic of pineapple fruit, such as appearance, color of skin and pulp and texture of pulp during storage in refrigerator. Moreover, the pineapple fruit will be classified the level of maturity by those characteristics.
2. To study the effect of pectin type, Ca-ion concentration, degree of esterification and pectin concentration on rheological properties. The rheological properties was measured by controlled shear rate examination and oscillation test
3. To study rheological properties of gums, such as guar, locust bean, xanthan gum. Moreover, effect of some factor, such as concentration and temperature on rheological properties of gum solution was considered to investigate. The rheological method was used in this study: controlled shear rate examination and oscillation test.
4. To study the synergistic effect between galactomannan, such as guar gum or locust bean gum, and xanthan gum on rheological properties of mixed gum solution. The study was focused on the effect of ratio between xanthan gum and galactomannan on rheological properties.
5. To study rheological properties of pineapple puree supplemented with selected gums, such as pectin, guar, locust bean gum, guar gum, xanthan gum. Effect of gums concentration and temperature on rheological properties of pineapple puree was considered to investigate. Shear rate examination method will be applied to determine the stability and viscosity of pineapple puree.
6. To study the synergistic effect of mixed plant gums (guar, locust bean gum) and microbial gum (xanthan gum) on stability and viscosity of pineapple puree. This study focuses on the ratio of mixed gum effect on pineapple puree. The stability properties were determined by controlled shear rate examination.
7. To compare the properties between produced pineapple puree and commercial puree products, such as baby food and apple puree products. The investigated properties included rheological properties such as controlled shear rate examination and oscillation test, pH, Total soluble solid.

Chapter 3 Review of Literature

Fruits contain minerals, vitamins and dietary fiber. They are also good sources of calcium, phosphorus, iron. Like vegetable play an importance role in human nutrition. They are vital sources of essential magnesium and contribute over 90 % of vitamin C. According to a report published by the National Research Council in both developed and developing nation supplies of fresh fruits and vegetables can be increased by as high as 30 - 40 % using technology to prevent their deterioration after harvest. (Nagy, 1980)

3.1. Pineapple

3.1.1 Introduction

The pineapple is one of number of agriculture food crops that were unknown to people of the eastern hemisphere before the European discovery and exploration of the Americans in the 15th and 16th centuries. By the time, the pineapple had already been developed by the native population from its indigenous South American ancestors into a cultivated food crops. At that time, the most export product was fresh fruit. (Robert, 1980). The major change in the economic importance of the pineapple occurred at the beginning of the present century when suitable canning techniques were developed and larger-scale pineapple production was begun. Production of canned pineapple and pineapple juice made the fruit available in many parts of the world too far removed from areas of cultivation for satisfactory shipment of the rather perishable ripe whole fruits.

Nowadays, Pineapple becomes the important topical commercial fruits of the world (Bartholomaw, Paul, Rohrbach, 2002; Chutintrasri & Noomhorm, 2005), particularly in the form of processed products. It is widely cultivated throughout the tropics and subtropics. (Table 3.1) It is important economic fruit crop in Thailand, the Philipines, China, Brazil, Hawaii, India, Mexico and South Africa (Table 3.2). Pineapple was cultured in the north, east and south of Thailand, in place such as Chonburi and Patanee Province. There are five varieties of pineapple in Thailand. The most popular variety is Pattavia variety which has the characteristic of being very sweet and juicy. The largest area of cultivation of this type is north of Thailand, for example, Lampang and Phetchaburi. The second one is intrachit variety which is the oldest variety in Thailand. This type is smaller than Pattavia variety, but its flavor is the same as Pattavia. Phuket variety is planted on the south of Thailand, Phuket province. This has the flavor of sweet and sour. Nangrare and Nomprang are planted in place of North of Thailand, but they are not popular.

Another area of cultivation for pineapple planting is Costa Rica in Middle of America and Brazil in South America. South Africa is also planted the pineapple fruit. Those countries are not export only fresh pineapple fruit. Importance processes of pineapple for export were canned, freezing and drying product.

Table 3.1 Production of Pineapple in different continents of the world (Salunkhe, 1995)

<i>Continents</i>	<i>Production MT</i>
World	9652
Africa	1191
North Central America	1380
South America	1213
Asia	5703
Europe	1
Oceania	163

Table 3.2 Major Countries Producing Pineapple (Salunkhe ,1995)

<i>Countries</i>	<i>Production MT</i>
Thailand	1865
Philippines	1170
China	790
Brazil	724
India	602
United States	522
Vietnam	490
Mexico	324
Indonesia	283
South Africa	265
Colombia	240
Malaysia	211
Kenya	202
Costa Rica	150
Zaire	143

3.1.2 Botany

Pineapple belongs to the family Bromeliaceae. There are two genera, *Ananas* and *Pseudananas*. The two genera include five species and one species, respectively. These are *Ananas bracteatus*, *A. fritzmulleri*, *A. comosus*, *A. eretifolius*, *A. ananassoides* and *Pseudananas saganaruis*. In Southeast Asia, the most popular contributing species have been planted and exported, was *Ananas comosus*. (Smith, 1995) The important commercial varieties in leading pineapple-growing counties are as follows in table 3. The syncarp of pineapple plant is well over 15 cm long at maturity. Floral breast are relatively inconspicuous, soon exposing the tops of the ovaries, and the flesh is palatable.

Table 3.3 Varieties of pineapple in some country (Salunkhe, 1995)

<i>Countries</i>	<i>Varieties</i>
Hawaii	Cayenne and Hilo
Philippines	Cayenne
Malaysia	Singapore Spanish
Australia	Cayenne and Red Spanish
Kenya	Cayenne
Mexico	Cayenne
Cuba	Cayenne and Red Spanish
Taiwan	Cayenne
Brazil	Red Spanish and Abacaxi
India	Giant Kew and Queen Maritius

Pineapple is a perennial herb which grows up to a height of 90-100 cm with a spread of 130-150 cm. (Figure 3.1) It bears a terminal inflorescence and fruit. Newly plants are known as the main crop, and those produced later from auxiliary 2 plants are called “ratoon crop”. In this way, the plant continues its growth and produces fruits for many years. Commercially, however, only one or two ratoon crops are taken.

Pineapple is a shallow-rooted crop, and the largest proportions of roots are found to have a soil depth of 30 cm. They are mostly confined to the lower portion of the stem. Roots are also present in the axils of the basal leaves. Moist conditions are required for the best root growth, are dry periods damage the superficially placed roots. The leaves are long and tapered toward the tip, and they are sessile. The lamina, through which the water percolates to the base of the plant, is shallow. The leaves bear a few marginal spines. However, the leaves of Queen Variety are spiny. The upper epidermal layer of leaves

consists of compact interlocking cells which are thickened and coated with waxy cuticle. Stomata occur only on the lower surface within longitudinal furrows. The lower and to a lesser extent the upper surfaces bear mushroom-shaped hairs known as “Trichomes”. The trichomes increase the thickness of the leaf surface and increase air resistance to the diffusion of gases and loss of water.

In general, flowering is irregular and is marked by an increase in the diameter of the meristem about 12-15 months after planting. The flowering period is observed to depend on the environmental conditions, type of planting material, and variety. Pineapple has a racemose type of inflorescence. About 100-200 flowers are found per inflorescence. They are hermaphrodite in nature. Every day about 5-10 flowers are observed to open. The opening of the flowers continues for a period of 10-20 days, starting from the base of the inflorescences toward the apex.

The fruit of pineapple develops parthenocarpically. It is a multiple type of fruit, formed by the fusion of berrylike fruitlets and subtending leafy bracts to each other and to the central fibrous axis or peduncle of inflorescence. Normally, the fruit is cylindrical, broad at the base and tapering slightly the apex. The time required from flowering to harvesting to harvesting of fruit is about 4.5-5.5 months. A crown of small leaves develops on the fruits. This crown can be used for propagation. It is formed by the continuous growth of peduncle. The apical meristem becomes narrower, and spiral leaves are produced. The growth of crown continues during fruit development, but it ceased at fruit maturity.



Figure 3.1 Pineapple

3.1.3 Composition

Freshly harvested pineapple fruit contains 86 % water, 8 g sugars, 0.5 - 1.6 g acids, 1 g proteins, 0.5 g ash, 0.1 g fats, some fiber, and vitamin (Mainly A and C). The vitamin C content varies from 10 to 25 mg/100 g. (Table 3.4). The range of chemical constituents of ripe pineapple depends on the stage of fruit ripeness, and on agronomic and environmental factor. The major carbohydrate constituents in pineapple fruits are simple sugars sucrose, glucose and fructose. There are no starch accumulations in pineapple fruit. The major acids in pineapple are citric acid and malic acid. The ripened fruit contains higher level of glycine, alanine, methionine and leucine, whereas lysine, histidine and arginine, are present at relatively low levels. Chlorophyll and carotenoids are the major pigments in green and yellow pineapple fruits. (Smith, 2003; Navy, 1980) Several volatile compounds were

identified in canned pineapple juice. These include acetic acid, 5-hydroxymethylfurfural, formaldehyde, acetaldehyde and acetane.

Table 3.4 Composition of 100 g of pineapple flesh (Smith, 2003)

<i>Constituents</i>	<i>Fresh peeled</i>
Proximate	
Water (g)	86.0
Energy (kJ)	158
Protein (g)	1.0
Fat (g)	0.1
Carbohydrate, total (g)	8.0
Sugar, total (g)	8.0
Starch (g)	0.0
Ash (g)	0.5
Cholestrorol (mg)	0
Acid, total (g)	0.5-1.6
Total nitrogen (mg)	45-120
Pigments, xanthoohylls (mainly carotniods) (g)	0.2-0.3
Dietary fibre (g)	2.0
Minerals (mg)	
Sodium	2.0
Potassium	180
Calcium	27
Magnesium	11
Iron	0.3
Zinc	0.2
Vitamins	
Retinol equivalents (µg)	4
Retinol (µg)	0
B-Carotene equivalents (µg)	25
Thiamin (µg)	40
Ribofalvin (µg)	30
Nicotinic acid equivalent (mg)	0.3
Nicotinic acid (mg)	0.1
Vitamin C (mg)	21

3.1.4 Storage

Fresh pineapple fruit is appreciated for its taste, flavor and juiciness. However, its shelf-life is limited by changes in color, texture, appearance, off-flavors and microorganism. The condition of storage is important effect for prolong the shelf-life of pineapple fruit or ripen the pineapple fruit. (Marta *et al*, 2008) Basically, the conditions have the temperature of storage and atmosphere.

3.1.4.1 Low-Temperature storage

As for many other fruits and vegetable, refrigeration aids shopping and extends storage life of pineapples. One haft-ripe fruit (smooth cayenne) can be held for about 2 weeks at 8.5-12.5 °C, gaining an additional 1 week of shelf life. (Smith, 2003) Mature green fruits (fruit picked with no yellow color showing on the shell) are susceptible to chill injury when store at temperature less than 10 °C. Py *et al*. (1957) recommended a storage temperature of 8.5 °C for South Africa pineapple. Endogenous brown spot frequently occurs

simultaneously with chill injury. This is not always the case, however, since storage at 8 °C for 1 week, followed by 1 week at 21 °C, frequently induces endogenous brown spot but not chilling injury. According to Dull (1975), at 7 °C, the maximum storage life was about 4 weeks. Freezing process considerably reduces the rate of the deleterious oxidative and enzymatic relations and also inhibits the growth of microorganism resulting in much safer product. (Bremer & Ridley, 2004) In a case of pineapple fresh cut, Marta (2008) suggested to preserve pineapple throughout 20 day at 5 °C, without being affected by the packaging conditions.

3.1.4.2 Controlled-atmosphere storage

The effects of different levels of carbon dioxide and oxygen on respiration and storage behavior of pineapples have been reported. Stage 4 fruits were placed in atmospheres containing air with 21, 10, 5 and 2.5 % oxygen. Nitrogen made up the balance of the atmosphere. The respiration rate decreased with decrease in oxygen concentration of the atmosphere. (Salvi & Rajput, 1995)

3.1.5 Pineapple products

3.1.5.1 Canned Products

Most of the world's pineapple production is canned. Slices are the most valuable product, followed by pineapple juice, chunks, and dried pineapple. Some other products are fruit salads, sugar syrup, alcohol, and citric acid. Canning is the most common preservation method used for pineapple. Collin (1960) and Obenland (2008) provided an excellent description of a typical small canning operation developed in Hawaii. In general, the fruits are sorted by side, shape, and freedom from major blemishes. The ends, i.e., the shell and core, are removed, yielding a cylinder of fresh which is cut into the usual slice, chunks, and smaller pieces. Fresh remaining on the trimmed shell and ends, as well as fragments from cutting operations, are used for extraction of pineapple juice.

3.1.5.2 Juice

Pineapple juice contains neutral polysaccharides composed predominantly of galactomannan. The de-gumming of juice can be achieved by using pectinase, cellulose, and hemicellulase preparation. The retention of ascorbic acid in bottled and sulfide juice and squash was 80-85 % at room temperature (24-30 °C) and only 38-47 % at 37 °C. Canned juice can be stored for 12 - 15 months without any serious loss in quality or nutritive value.

3.1.5.3 Concentrate

Pineapple juice concentrate can be prepared by various methods, with or without neutralizing the excess acidity. It can be prepared under vacuum and fortified with ascorbic acid. Aroma concentrate from pineapple juice can be separated and later added back to striped juice concentrate to obtain fully flavored concentrate. (Table 3.5) The concentrate with added aroma was comparable to fresh juice concentrate could be stored satisfactorily at 10 - 38 °C with the addition of SO₂ without causing any undesirable change in color or flavor.

3.1.5.4 Powder

Attempts have been made to prepare powder from pineapple juice by freeze-drying. Giant Kew variety of pineapple with a minimum 12 °Brix, acidity around 1.0 %, and with a minimum of 120 µg total carotenoids per 100 g juice (Table 3.5) was found to yield a product of acceptable quality.

3.1.5.5 Waste Products

Several products such as bromelain, wine, sugar syrup, citric acid, wax, sterols, and cattle feed can be produced from the mill juice of pineapple processing industry waste.

Table 3.5 Chemical analysis of aroma and stripped pineapple juice concentrate (Phanindrakumar, 1991)

Sample	Ester ($\mu\text{g}/100\text{ g}$)	Carbonyls ($\mu\text{g}/100\text{ g}$)	Alcohols ($\text{mg}/100\text{ g}$)	Oxygenated Terpenes ($\mu\text{g}/100\text{ g}$)	COD* ($\text{mg}/100\text{ g}$)
Fresh feed juice	15.0	2.00	0.180	0.303	10.70
Aroma concentrate	11.9	1.58	0.140	0.240	8.60
Stripped juice concentrate	1.2	0.16	0.150	0.025	0.85
Stripped juice concentrate with aroma added back	12.0	1.60	0.150	0.270	9.40

*Determination of chemical Oxygen Demand

3.2 Pectin

Pectin is the natural polymers (structure material) which found in all land plant. Like starch and cellulose, pectin is a structural carbohydrate. Pectin was found in the 18th century and the first characteristic to be applied in food products, was gel formation. Commercially, pectin is extracted from citrus peel and apple pomace. (Brent, 2000; Visser & Voragen, 1996)) Pectin is used as a gelling agent in traditionally manufactured fruit-based products, especially jams and jellies.

3.2.1 Structure

Commercial pectin are composed mainly of polymerized, partly methonolesterfied (1-4)-linked α -D-galacturonic acid. (Stephen, 1995) (Figure 3.2) The pectin molecule can contain 200 - 1000 linked galacturonic acid units. In some pectins, the methylester groups are partially replaced by amide groups, to a maximum of 80 %. During extracted by non-degradative means, dilute acids are generally used. Therefore, the structure of the resultant pectin differs greatly. About 5 - 10 % of the galacturonic acids are neutral sugars such as galactose, glucose, rhamnose, arabinose and xylose. They can be bound to the galacturonate main-chain (rhamnose) or be a part of contaminating polysaccharides (glucans and xyloglucans). Pectin from apple, citrus, cherry, strawberry, carrot, pumpkin, sugar beet, potato, onion and cabbage have the same neutral sugar composition. In contrast, pectin from mountain pine pollen, Japanese kidney beans and duckweed which contain large amounts of xylose or apiose.

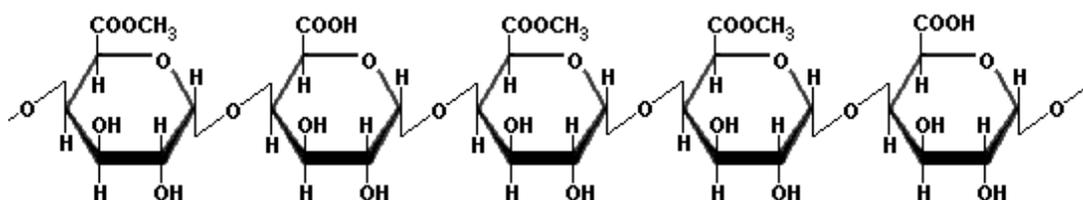


Figure 3.2 Polymer structure of pectin (Seymour, 2002)

3.2.2 Sources and properties

Pectin can differ as a result of ripening and these differences can influence the efficiency of the extraction process. Pectin extracted from the primary cell wall may have

more branch of neutral sugar than that extracted from the middle lamella. Side-chains (neutral sugar side-chains) are distributed unevenly along the main-chain. Therefore, models describing smooth and hairy regions within pectin that has been extracted by a mild process can be deduced for pectin substances from citrus, sugar beet, cherry and carrot.

3.2.3 Pectin manufacture

Pectin production depends on a number of factors, including access to raw material, water, energy and effluent disposal at reasonable prices. In contrast to many other hydrocolloids, no crop is grown or harvested with the primary aim of producing pectin. Like, gelatin, pectin is produced essentially from waste materials, and is dependent on the operations of the primary industry of juice production. Hence the availability of raw materials, and its quality, is large dependent on the market for various types and qualities of juice and, to a lesser extent, essential oils. Some area, such as Brazil and to agree Florida, large quantities of fruit are grown specifically for juice production, but these are fortunately very suitable for pectin manufacture.

The present structure of the industry has been created by combination of these factors. In the USA, apple pectin produce, apple pectin producers had higher production costs than those of citrus pectin. More recently, environmental restrictions in California have caused the closure of the pectin production, because of the cost both of effluent treatment and of water supplies. In contrast, European pectin plants, founded to produce apple pectin, have been expanded by importing dried citrus peel from a variety of sources. This has given a degree of production against poor harvests in any one area.

3.2.4 Pectin Production

Commercial pectins are almost exclusively derived from either citrus peel or apple pomace: both by-products from juice (or cider) manufacturing. Apple pomaces contain 10 - 15 % of pectin on a dry matter basis. Citrus peel contains 20-30 % of pectin. Citrus and apple pectins are largely equivalent from an application point of view. Citrus pectin are light cream or light tan in color, but apple pectin are often darker.

Suggests alternative sources include sugar beet waste from sugar manufacturing, sunflower heads (seed used fro edible oil), and mango waste. Sugar beet pectin was produced in England and Germany during the 2nd World War and in Sweden and Russia in the following years. Sugar beet pectin is inferior to citrus or apple pectin in all presently significant applications, owing to (1) presence of acetate esterification, (2) a relatively low molecular mass, and (3) presence of large amounts of neutral sugar side chains.

Pectin production is outlined in Figure 3. Two general processed are used; (1) separating the pectin from most other water-soluble material by precipitation with an alcohol and (2) those precipitating the pectin as an insoluble salt with suitable multivalent metal ions. Both processed can be used to obtain an pectin within the 2 main groups, namely, HM-pectin and LM-pectin.

3.2.5 Modification of pectin

When first extracted has a relatively high degree of esterification: around 70-75 % of the acid groups in the molecule being naturally esterified with methanol. Such pectin is ideal for use in a conventional jam, and will give a rapid set to prevent the floating of fruit. However, other uses require the preparation of pectins with different setting characteristics. Pectin is modified by reducing the degree of esterification (commonly referred to as DM or degree of methylation). This is most commonly carried out by acid hydrolysis.

This can be carried out at several stages of the process, in either raw material, the extraction process, the concentrated extract or the wet precipitated pectin. Alternative processes could be to use alkali at low temperatures, purified pectin esterase or ammonia. If ammonia is used, some of the ester groups are converted to acid amide group (-CONH₂), producing an amidated pectin.

If the DM is reduced to around 60 %, the pectin is a slow-set type, and is capable of gelation only in high-sugar systems. Under similar conditions, the gel will set more slowly or at a lower temperature than with the original rapid-set pectin. However, it also will tolerate either higher sugar concentrations or a lower pH. Once the DM is below 50%, the pectin are known as low methoxyl, and become steadily more reactive with calcium. They can be gelled under progressively lower soluble solids conditions, provided an appropriate amount of available calcium is present. Amidated pectins are mostly of the low methoxyl type, and have the advantage of tolerating more variation in calcium content.

3.2.6 Properties of pectin

3.2.6.1 Gelation mechanisms of pectins

Pectin is divided into 2 groups by the mechanism system which are HM pectin (High methyl ester pectin) and LM pectin (Low methyl ester pectin). Each type of pectin performs difference properties, such as a rate of gel setting, but it is depend on a preparation method. The condition of pectin preparation affects with the gel properties and gel performance, e.g. value of pH, level of Ca ion. (Table 6) (Alstair, 1995)

3.2.6.1.1 HM-pectin

An ability of HM-pectin to form the gel with sugar and acid called low is called low-water-activity-gel or sugar-acid-pectin gels. Such a gel is considered as a three-dimensional network of pectin molecules in which the solvent (water) with co-solutes (sugar and acid) is immobilized, resulting in a system resisting deformation and showing a stress/stain relationship for small deformations. The rheological behavior under strains used for testing (finger feel, instruments) and use (spreading, mouthfeel) is interpreted as rubber elasticity, with a low young modulus. Rubber elasticity implies the presence of long chain molecules that can form statistical coils between so-called "junction zones" in which there are chain associations and by which the three-dimensional network is build up. Junction zone formation is made possible by the local conformation of the pectin chains and brought about by the co-solutes. The high sugar concentration creates condition s of low water activity which, in turn, promotes chain-chain rater than chain-solvent interaction, whereas the acid lessens the negative changes on the carboxyl groups, thus diminishing electrostatic chain repulsion. The fact that sucrose can be replaced by other polyols, that are less acid, is necessary for pectin with higher DM.

3.2.6.1.2 LM-Pectin

Pectin with low methoxyl content ($DM < 50\%$) can gel in presence of divalent cations-calcium for food gels. Gelation is due to the formation of intermolecular junction zones between homogalacturonic (“Smooth”) regions of different chains. The structure of such a junction is still controversial because the “egg-box” binding (Figure 3.4) process implies the formation of 2_1 helices while only 3_2 helices have been shown on dry calcium pectate gel by x-ray diffraction. In LM-pectin, there are interchain hydrogen bonds between undissociated carboxyl groups. (Einhorn-Stoll & Kunzek, 2009)

Because of the electrostatic nature of bonds, pectin gels are very sensitive to intrinsic parameters that can modify the environment of the carboxyl groups, such as nature distribution, and amounts of substituents along the galacturonic backbone. Thus the gel-forming ability increases with decreasing DM, and LM pectins with a blockwise distribution of free carboxyl groups are very sensitive to low calcium levels. The affinity of pectin for calcium is decreased by acetylation, and a poor gelling power is found for beet pectins. In contract, amidation increases or improves the gelling ability of LM-pectins: amidated pectins need less calcium to gel and are less level to precipitation at high calcium.

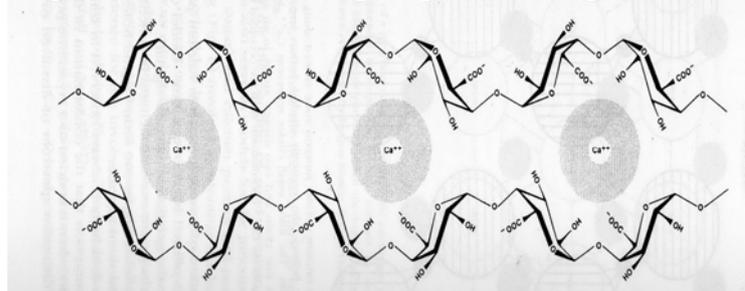


Figure 3.4 “Egg-box” model of junction zone in calcium pectate gel (Christensen,1986)

Table 3.6 Condition of gel setting for pectin (Stephen, 1995)

<i>Pectin types</i>	<i>DM</i>	<i>DA</i>	<i>Gelling condition</i>	<i>Setting rate</i>
High-methoxyl	74-77	0	Brix >55 pH < 3.5	Ultra rapid set
High-methoxyl	71-74	0	Brix >55 pH < 3.5	Rapid set
High-methoxyl	66-69	0	Brix >55 pH < 3.5	Medium rapid set
High-methoxyl	58-65	0	Brix >55 pH < 3.5	Slow set
Low-methoxyl	40	0	Calcium ions	Slow set
Low-methoxyl	30	0	Calcium ions	Rapid set
Amidated low-methoxyl	35	15	Calcium ions	Slow set
Amidated low-methoxyl	30	20	Calcium ions	Rapid set

3.2.6.2 Solubility and viscosity

Pectin is soluble in cold water and gives a Newtonian behavior. Like other viscous gums, it needs care in dispersing the powder rapidly into water; lumps of powder easily become coated with gel layer which makes further dissolving slow and difficult. It is important therefore to adopt a technique which facilitates dispersion to the individual particle level. This can be achieved either using a high-shear mixer, or by diluting the pectin with

a soluble solid, such as sugar. Because pectin is only very slowly soluble in concentrated sugar solutions, it is possible to disperse the powder easily into syrup and then to dilute this with water to below 20% total solid, when the pectin will dissolve on heating with only gentle stirring.

Although pectin is viscous in solution, it is not the most viscous of gums, and it would not usually be chosen where an increase in viscosity is the only desired effect. However, where only a small increase in viscosity is required, for example to replace the mouthfeel of sugar in a low-calorie drink, pectin can prove very effective. (Imeson, 1994)

3.2.6.3 Stability of pectins

The behavior of pectin in acid and neutral environment determines its functionality as a neutral constituent of many plant materials and its use as an additive in food production for gelling and thickening. The stability of HM-pectin and pectin acid at various pH values, expressed as residual viscosity of buffered after heating for 10 minutes at 90 °C. HM-pectin solutions are most stable at pH 3-4. At lower, pH, even at low temperature, methoxyl and acetyl groups are removed and the neutral sugar side chains hydrolyzed. With increasing temperature these reaction accelerate, and hydrolytic cleavage of the glycosidic bonds in the galacturonan backbone takes place progressively. At higher acid concentrations monogalacturonic acid will be degraded to CO₂, furfural, and, other products. The CO₂ production which is quantitative on boiling in 12 M hydrochloric acid, can be for estimation of pectin. Einhorn-Stoll & Kunzek (2009) investigated the thermoanalytical characteristic of processing independent structural change of citrus pectin. Pectin is stabilized by inter- and intra-molecular attraction forces, such as hydrophobic interactions and hydrogen bonds.

3.2.6.4 Degradation

The pectin molecule is quite easily degraded. Although pectin, in contrast to other gums, is fairly stable under acid conditions, its chemical structure makes it prone to breakdown under less acid conditions, at a pH of 5 or above, especially at higher temperatures. Because the reaction can occur wherever there is an esterified acid group in the molecular chain, a small amount of degradation can give a large loss in viscosity, gelling power and other functional properties. The rate of degradation is less with low methoxyl pectins, and virtually absent in pectic acid, the fully de-esterified material, and its salts. Hence, only pectic acid or pectins of very low degrees of esterification can be used in neutral products, especially those which are to be heat processed. (Imeson, 1994) Thermal degradation was generally used to pectin. Godeck, Kunzek & Kabbert (2001) found difference in thermal degradation behavior in dependence on the degree of methoxylation (DM) of pectin component.

3.2.6.5 Factor affecting of pectin

Applications of pectin are based upon their ability to form gels. Gelation will, however, only occur under certain conditions. Factors that determine whether gelation can occur and influence the characteristics of gel include temperature, concentration of pectin, pH, concentration of sugars, and concentration of ions, such as Ca²⁺. (Whistler, 1993)

3.2.6.5.1 Temperature

A pectin gel is in most cases prepared hot and then solidified by cooling. When cooled below the gelation temperature, systems containing LM-pectin will gel almost instantaneously whereas HM-pectin systems will gel after a time lag. Once formed, an HM-

pectin gel cannot be remelted, but an LM-pectin gel can, in most case, be remelted and reformed repeatedly, i.e., it is usually thermo-reversible.

Commercial pectins are standardized to reproducible gelation temperature or gelling time under certain conditions given in the standardization procedure (subsection titled Gelling Time and Gelling Temperature). Attention must be paid to the gelation temperature because of the risk of pre-gelation, i.e., gelation before the manufacturing process has been completed. Mechanical disturbance of the system while gelation is in progress will result in broken gel that is often confused with weak gel. It is, on the other hand, often desirable to fill commercial containers at temperature close to gelation temperature to prevent flotation of particle.

3.2.6.5.2 pH

A pH of about 3.0 - 3.1 is typical for high-sugar jams (HM-pectin). Low-sugar jams may be slightly less acidic for taste reasons. A decrease in pH within the vicinity of these values usually favors gelation; the gelation temperature increases or both HM- and LM-pectin gels and the setting time is reduced for HM-pectin gels. Low pH value also tended to increase the strength of both HM- and LM-pectin gels. Gels will generally not form above about pH 3.5 in the case of HM-pectin and about pH 6.5 in the case of LM-pectin. These limits are, of course, dependent on other factors. Among the HM-pectin, those with lowest DE need lower pH for their gelation than do the more highly esterified HM-pectins. Glucose syrup is used in place of sucrose and it is thus more difficult to control the rate of setting in this case.

3.2.6.5.3 Concentration of pectin

Typical concentrations of pectin in jam and jellies range from 0.3 % (HM-pectin gelling) to 0.7 % (amidated LM-pectin gelling); the pectin concentration used is inversely related to the concentration of solution solids. At fixed levels of all other parameters, increasing the amount of pectin causes the gel strength of the resulting to increase.

3.2.6.5.4 Degree of Esterification

DE values for commercial LM-pectin typically range from 20 to 40 %. Those with the lowest DE-values show the highest gelling temperatures and the highest sensitivity to (smallest requirement for) Ca^{2+} . In contrast, the highest gelling temperature and fastest gelation of commercial HM-pectins are found with those that have the highest DE. This is reflected by the subdivision of commercial HM-pectin into rapid-set (70-75 % DE), medium-rapid set (65-70 % DE), and slow set (55-65 % DE) pectins. Slow set pectin may form gels as strong as the gels formed by rapid-set pectins, but they need lower pH for their use.

3.2.7 Interaction of pectin with other food constituents

3.2.7.1 Interaction between Alginate and pectin

In order to generate new rheological properties, mixtures of established polysaccharides have been investigated: among such synergistic mixtures (Carob-Xanthan, Carob-Agar, Carob-K-Carrageenan), pectin-alginate systems have been studied. The interactions between alginates and pectin depend mainly on the mannuronic/guluronic acid ratio of the alginate, the DM of the pectin, and the pH. Gels with good properties are obtained with high-methoxyl pectins and guluronic acid-rich alginates; the pH is also important, and a pH greater than 4 completely hinders the gelation. This fact, together with the gelation of low-methoxyl pectins and alginates under very acidic conditions (pH < 2.8), indicates that the chains must be sufficiently unchanged before interaction can occur and that

esterification is required only to reduce electrostatic repulsion. These interactions are claimed to be specific rather than based on incompatibility or exclusion effects and are ascribed to the packing together in rigid ribbons of the polyguluronic acid and methyl ester regions of the pectins. These mixed systems may be used, when cold-setting of gels is required. (Morris, 1984)

3.2.7.2 Interactions between Pectin and Proteins

The interactions between proteins and polysaccharides are thought to be essential for satisfactory food texture. Mixtures of polysaccharides and proteins may exhibit incompatibility or form soluble or insoluble complexes, and the conditions leading to complexation or phase separation depend on the physical/chemical properties of proteins and polysaccharides as well as the physicochemical environment (pH, ionic strength, nature of the ions, temperature etc.) (Totstoguzov, 1991) Einhorn-Stoll *et al.* (2005) investigated formation of pectin and milk protein conjugates. The amphiphilic milk proteins normally act there as emulsifiers and the strongly hydrophilic pectin as stabilizing or thickening agent. They found that the type of milk protein has most influence with conjugation.

3.2.8 Applications in Food systems

Pectins find use as gelling agents in fruit preserves before they were ever isolated in pure form. It is, therefore, that at present the world's production of pectin is still mainly used as a gelling agent for jam and jellies, to compensate for the deficiency of natural pectin in the fruits themselves. Original jam is generally made from high-ester pectin, whereas the low-ester pectins are used when a softer, more spreadable texture is desired. If fruit particle (pulp) is to be contained in the jam, a high gelation temperature is used and solidification begins almost immediately after filling the containers, with almost no floatation of the particles being observed.

To prepare low-sugar (less sweet) gums, low-ester pectins are used in combination with calcium in an amount related to gelation temperature and the quality of the formed texture. When jellies that contain no particles are produced, slow-setting pectins those solidify a long time after filling, allowing air bubbles to float and escape from the product, are preferred. (Rolin & De Vries, 1990) For confections, slow-setting high-ester pectin is used.

Pectins are used to prepare bakery filling and glazes. Oven-resistant high-sugar jams are produced at a solid content of ~70 % using rapid-set pectin. Another demand of such products is mechanical stability. The less the gel is ruptured, the lower the syneresis at elevated heating temperatures. Non-amidated low-ester pectins are recommended for the production of bakery jam with satisfactory stability. Low-ester-pectin gel is produced with ~65 % soluble solids and a relatively high dosage of calcium-reactive, low-ester pectin. (Nussinovitch, 1997)

Pectin also applies for stabilization of pasteurized or sterilized, acidified milk products (pH values of ~ 3.5 - 4.2). It can be achieved by using high-ester pectin with DE greater than ~ 70. Acidification can be produced by either fermentation or the addition of fruit juice. It casein stabilization is not achieved; an undesirable grain-like texture is obtained. The pectin, added before homogenization, is absorbed onto the casein particles, which have a positive charge in the unstabilized milk. If the amount of added pectin is small, then the charge is neutralized and the system tends to collapse owing to the removal of repulsive forces. (Nakamura, 2006)

Pectin is also used to stabilize clouding in beverages. Such stability is dependent on the nature and amount of the pectin present. Natural clouding agents can be produced. (Elshamei and Elzoghbi, 1994) from orange and lemon peels using enzyme preparations to hydrolyze the pectin in the peel. The chemical and physical properties of the clouds were evaluated in parallel to the drink's properties, taste and stability. The cloudiness of the produced drinks stabilized after 42 days storage at 25 °C.

3.3 Seed gums

With a few exotic exceptions, life on earth depends on the energy captured by photosynthesis in plants and algae. The sun does not shine all the time and therefore photosynthesis organisms require some chemical form for storing energy. The small amounts of energy are to be stored small molecules, such as monosaccharide. In seed, relatively large amounts of energy must be stored to guarantee survival of germinating plant and here the use of simple sugars has certain limitations. The sugar in seed is may be polymerized and stored as polysaccharides. The galactomannans are one such group of polysaccharides.

3.3.1 General of galactomannans

Typical, leguminous plants contain small amounts of galactomannans in the cell walls where presumably they have structural function. In some species these polysaccharides have replaced starch as the reserve polysaccharides in the seeds. The deposition of galactomannan occurs in and on the walls of endosperm cells, progressively filling these cells and in some species completely excluding the cytoplasm. In contrast to starch, the depot is outside the cell membrane and the enzymes responsible for its ultimate degradation are produced by other cells within the seed. Currently, galactomannans from three species, such as guar, locust bean and tara gum, are exploited as food additive.

3.3.1.1 Locust bean gum

The locust bean plant (*Ceratonia siliqua*) is an evergreen tree (Figure 3.5) originally indigenous to the Middle East, which was cultivated and spread by the early civilizations that flourisher around the Mediterranean. In autumn the tree bean sugar-rich pods which make an excellent animal feed. The tree thrives on rock, semi-arid soil. It yields fruit 5 years after budding and reach maturity at age of 50. (Rol, 1973) The pods are 10-20 centimeters long and each contain 10-15 seeds or carob beans, that are the source of polysaccharide

LBG is considered a GRAS (Generally recognized as safe) food ingredient by the FDA (American food and drug Administration). The maximum allowable concentration in USA is 0.8%, in cheese under regulation 101.04 of this code, the gum's addition to a food product must be specified on the product's a label where ingredients are listed in descending order of predominance (Federal Register, 1987).



Figure 3.5 Botany of locust tree, pods and seeds

3.3.1.2 Guar gum

Guar gum is obtained from the seeds of *Cyamopsis tetragonolobus*, which has been cultivated for centuries by the farmers in the arid semi-desert regions of northwest India (Rajasthan) and Pakistan as fodder. The guar pods are used there for animal feed and human consumption. The guar plant is a fast-growing annual (~ 1 m high)(Figure 3.6), planted after the monsoons in June/July and harvest in December. The pods are green, each one containing six to nine pea-shaped seed, which are ~2-4 mm in diameter and weigh approximately 35 mg each, of which ~36 % is galactomannan (Herald, 1986). (Figure 3.7)



Figure 3.6 Guar plant



Figure 3.7 Guar pods and bean

With the onset of drought the plants die and the pods turn light-brown in color. The pods are harvested by hand from the plant, except in Texas where mechanical harvesters are employed. From non-irrigated land yield of about 200 kg seed/hectare can be expected, giving an annual income of £20. Manufacturing includes separation of the endosperm from germ and the testa, and grinding to compose the gum. The gum is available in a wide range of sizes, which affect their solubilization rates. Thermal degraded gums with reduced viscosities are commercially available. Streamed powders exhibit an enhanced dissolution rate and a reduction in their typical tastes. Two major grades of guar gum are marketed, food and industrial. For industrial purposes, ground endosperm is used, including small amounts of hull and germ resulting from imperfect purification. The industrial grades are manufactured with chemical additives, such as carboxymethyl, hydroxyalkyl and quaternary amine derivatives, to manipulate functional properties such as viscosity, solubility and swelling.

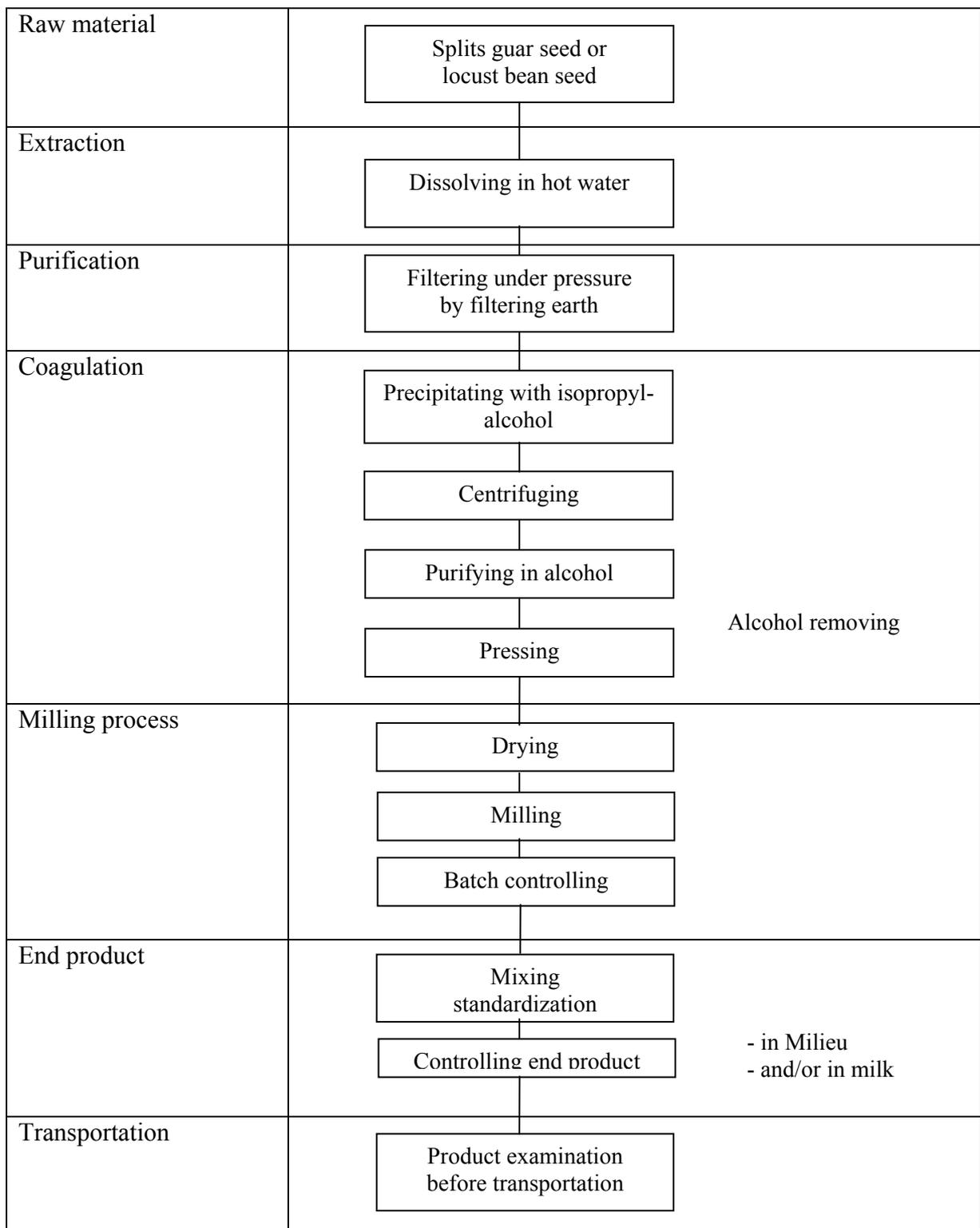
Guar gum is regarded as GRAS by the FDA (Federal Register, 1987) and by other world wide regulatory agencies. The maximum allowable concentration of guar in food is 2% by weight, as found in vegetable products and in fats and oils. The gum's presence in foods must be listed on the label. Guar gum solutions are sometimes used as model for Non-Newtonian liquid foods. (Anantheswaran and Liu, 1994; Blond, 1994)

3.3.2 Production of Galactomannans

For the production of locust bean gum, ripe brown pods which fall or are knocked off the trees are collected in September/October. The pods are broken into pieces to recover the seeds in a process known as kibbling. The seeds are covered with a dark-brown seed coat or testa which is firmly bound to underlying galactomannan-containing endosperm and which must be removed before grinding. The original production process involved treating whole seeds with concentrated sulphuric acid to "burn" off (or dissolve) this cellulose layer. Owing to environment problem associated with the disposal of waste acid, almost all production is now carried out using the alternative thermal process. The beans pass through a high-temperature oven and are broken using special mills while hot. During heating the testa becomes brittle and most springs away from the more pliable endosperm in mill. This creaking process also frees the germ, which lies between the two endosperm halves in the seed. The freed germ, endosperm and testa are subsequently separated and the endosperms ground to make commercial locust bean powder. Another alternative process for locust bean gum production, as according to Cargill, Incorporated, is separated into two phases, which are flour and extraction manufacturing processes. (Figure 3.8)

Generally, the higher the yield attempted in grinding the more specks will be present in the powder. Because of this, less than 30 % of the seed weight is recovered as food-grade galactomannan. The remaining 10 % of galactomannan, which has a high speck level, is sold as technical grades. The germ and testa, which together represent about 50 % of the seed, are sold with the kibbled pod as animal feed. The standard gum is sold in range of particle sizes, the coarser powders giving a slightly higher viscosity. (Fox, 1994)

Product: Galactomannan



Pure Guar		VISOGUM
Guar mixing	with Carragenan	LYGOMME – FLANGEN - GELOGEN
	with Alginate	SATIALGINE
Locust bean	with Xanthan	SATIAXANE

Figure 3.8 Galactomannan production (Mero – Rousselot – Satia, 2000)

3.3.3 Galactomannan structure

Galactomannans are linear polysaccharides based on a backbone of β -(1-4)-linked D-mannose residues. Single α -D-galactose residues are linked to chain by C-1 via a glycosidic bond to C-6 of mannose. Screening gum from a single source verifies that it is not a single substance, but contains molecules with different degrees of polymerization. (Lopes da Silva and Goncalves, 1990) The degree of galactose substitution varies from one botanical source to next as well as between molecular species of one gum. LBG with an average ratio of 1:4 (Figure 3.9) compared with guar (Figure 3.10) with an average ratio of 1:2. According to Table 3.7, this is manifest in the difference between weights of and the number –average molecular weights of galactomannans obtained from these gums. The M_w values of LBG and guar gum are similar 1.96×10^6 and 1.9×10^6 , respectively, whereas the M_n values are ~ 80000 for LBG and ~ 250000 for guar gum.

Table 3.7 Comparison of the composition of galactomannans (Imeson, 1994)

Galactomanan source	Average galactose to mannose ratio	\overline{M}_w Daltons	\overline{M}_n Daltons	Intrinsic viscosity (dl/g)
Guar gum				
High molecular weight	1:2	1.9×10^6	250,000	14.0
Low molecular weight	1:2	0.4×10^6	-	4.5
Locust bean gum	1:4	1.94×10^6	80,100	10.0

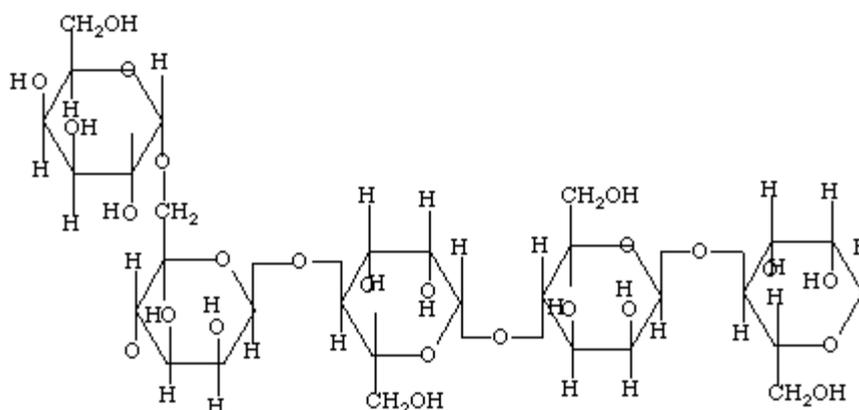


Figure 3.9 Structure of locust bean gum (Harper, 2006)

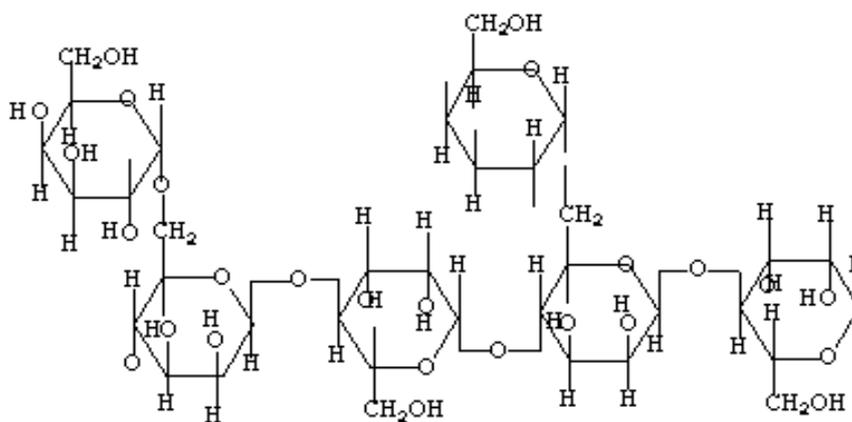


Figure 3.10 Structure of guar gum (Harper, 2006)

Carob gum has a ‘black’ structure, i.e. branching units clustered mainly in block of ~25 residues (‘hairy’ region), followed by even longer blocks of unsubstituted β -(1-6)-D-mannopyranosyl units (‘smooth’ region). The latter are important in the formation of interchain associations. (Dea, 1979) Since separation of testa and endosperm is limited, impurities can be found in commercially sold gum. These include 4 % pectosan, 1 % cellulosic material, 1.1 % ash and 6 % proteinaceous material. The last is in part covalently bound to the polysaccharide. Major amino acids are present in the proteinaceous component of LBG; in decreasing order of abundance these are glutamic acid, aspartic acid, glycine, arginine, alanine and serine (Anderson, 1986)

Unlike LBG, guar gum possesses a regular, alternating structure (Dea *et al.*, 1977). It can be schematically presented by its regular, twofold conformation. The unsubstituted D-mannopyranosyl units represent the so-called ‘smooth’ side, while the substituted D-galactopyranosyl units constitute the ‘hairy’ side. This conformation explains guar gum’s functional properties.

To improve and diversify its commercial applications, guar gum was modified by introducing changes in its chain structure. Properties of the carboxylated polyelectrolyte obtained from guar gum were studied. The changed macromolecules formed from native guar showed all the typical characteristics of polyelectrolyte. Viscometry results indicated that carboxylated guar had much higher viscosity in low salt-content medium than the native polymer, which improved its thickening properties (Frollini *et al.*, 1995).

3.3.4 Properties

3.3.4.1 Solubility

Mechanism of solubility, D-mannose differs from D-glucose only in the stereochemistry at C-2. Therefore, it can be said that D-mannan is an insoluble fibrous material similar to its D-glucose analogue, cellulose. This behavior is attributed to the formation of stable crystalline regions in the solid in which the linear chains lie in close proximity. The inclusion of side chains spoils this crystallinity and thereby promotes the penetration of water and enhances solubility. Thus, commercial gums showing high substitution ratio, such as guar, tend to hydrate fully in cold water, while gums with limited substitution, such as locust bean gum, hydrate completely only in hot water. Commercial gums exhibiting high substitution ratio (i.e. guar gum) are better hydrated in cold water than gums with limited substitution (i.e. LBG), because the presence of side chain interferes with the formation of stable crystalline regions and promotes water penetration, thereby enhance solubility. This behavior is reflected in the viscosity of the hot- and cold-prepared solution. Galactomannans don’t hydrate instantaneously in water. At 25°C, guar gum may require up to 120 min hydrate fully and yield its maximum potential viscosity. This time can be shortened by using a high-shear mixer, a fine powder or by increasing the temperature. However, at temperatures above 80 °C, thermal degradation becomes significant and the maximum potential viscosity will not be achieved. The rate and degree of hydration may be dramatically reduced by the presence of other solutes. When using galactomannans in formulated food, it is good practice, therefore, to hydrate these first in any free water present in recipe before adding the remaining ingredients.

3.3.4.2 Stability

When galactomannans are used as thickeners in processed food, sterilization (120 °C for 10 min) under neutral conditions results in a ~10 % loss in viscosity. This situation can

be improved by the addition of trace elements such as sodium sulfite and propyl gallate, suggesting that the dominant mechanism is reductive-oxidative depolymerization. The mechanism only applied at pH values >4.5 . At low pH, hydrolysis of the glycoside bond results in $\sim 90\%$ loss in viscosity when the solution is heated to $120\text{ }^{\circ}\text{C}$ for 10 min. Therefore, the buffering of processed systems as well as a degradation, and hydration can be delayed by using coarsely ground galactomannan powder. Galctomannans are generally stable to shear forces unless extreme conditions are used during processing, such as those in high-pressure homogenization (Fox, 1992)

3.3.4.3 Viscosity

The industrial use of galctomannans is primarily a result of their ability to produce highly viscous aqueous solutions at relatively low concentrations (Goldstein *et al.*, 1973). When galctomannans are dissolved in water the long mannan chain unfolds to form a open, flexible non-ordered conformation termed a random coil. (Morris and Ross-Murphy, 1981) At low concentrations these coils are well separated and free to move and change their orientation or shape within this solvent. This can be termed the dilute domain and within it the viscosity of the solution of the solution increases with concentration of polysaccharide in a linear manner. (Einstein, 1906) Pablyana et al (2005) studied the viscosity of hydrogel of guar gum with difference preparation, such as used the salt buffer as solvent. The viscosity of guar gum showed the decreased with increasing shear rate. Thus, guar gum solution behaves as structure fluid behavior in buffer salt solution, shown in figure 3.11.

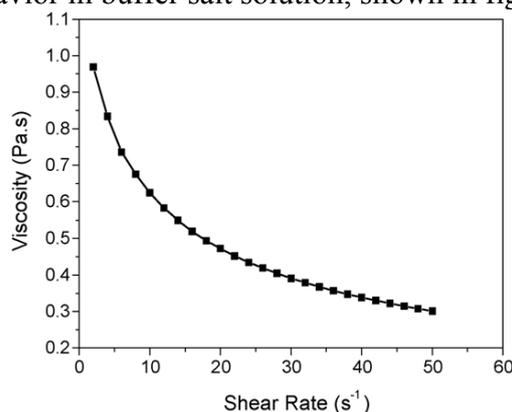


Figure 3.11 Effect of shear rate on viscosity of guar gum solution in NaCl buffer (0.8 % of gum concentration, $25\text{ }^{\circ}\text{C}$) (Pablyana, 2005)

For galactomannans and many other polysaccharides which form extended random coils in solution, $[\eta]$ is larger and the above does not apply. Such solutions exhibited structure viscous behavior (Figure 3.12) where viscosity falls with shear. In the mouth such thickened solutions appear to thin on mastication and give a pleasant, light mouth feel. This shear thinning can be explained by disentanglement of the polysaccharide 'Felt'. As the speed of shear increases with respect to the speed of absolute resistance) falls. Once shear ceases, re-entanglement is immediate and the solution exhibits its original low show shear viscosity. In this respect galactomannan differ fundamentally from starch pastes, which also exhibit pronounced shear thinning, but which, once sheared, lose viscosity permanently.

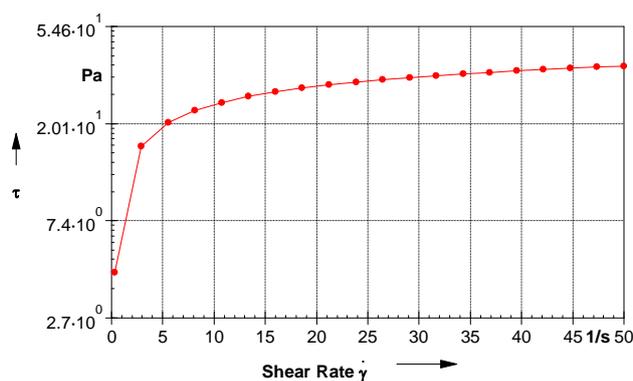


Figure 3.12 Flow curves of all gums (except xanthan gum)

3.3.5 Application of galactomannan

Galactomannan are used for their inherent properties; the most widely exploited being the thickening of aqueous solutions. Other desirable properties include their synergistic interaction with other polysaccharides and their ability to reduce syneresis. (Glicksman, 1969) For thickening purposes, low concentrations of 0.5 - 1 % are used. The galactomannans produce a light texture, recover after shearing, some of them are cold-soluble and viscosity is dependent temperature.

For stabilization purposes, galactomannans are used commonly in ice cream, compare with the use of seed gum in other milk-base products, which is limited by protein-phase separation. To an ice cream mix that include milk fat, non-fat milk solids and added sugar, 0.5 % mono/di-glyceride is added (to destabilize the protein layer around the emulsion fat globules) with 0.3 % high-viscosity LBG or a mixture of guar-LBG. Later on during cooling and whipping, partial churning of the fat occurs, and the free liquid fat with fat crystals forms a stabilizing layer around air pockets within the mass. The role of the galctomannans in the ice cream is to inhibit growth of larger ice crystals, by binding the fluid water to the gum and thus preventing its mass transfer, and to thicken, yielding a product with a creamier mouthfeel. Ice-crystal size on soft, flavored ices is reduced by adding ~ 0.1 % of galactomannans. As previously mentioned, guar gum combined with LBG or carrageenan prevents the formation of large lactose and ice crystals (Fox, 1992)

In fermented milk products, the addition of gum mixture composed of CMC, galctomannan and gelatin is used to overcome the problem of structure loss, when fresh cheese is sheared by regular processing. In milkshakes, less than 0.1 % galactomannan is used to thicken and impart a creamier mouthfeel to the product. Galactomannans are also used in milk-fortified fruit-juice drinks where the proportion of milk is low, to delay sedimentation of the casein micelle and ensure acceptance of the product.

Galctomannans, in addition to their use in gelled desserts base on carrageenans, are helpful in modifying gel texture and preventing syneresis. (Herald, 1986) A gel dessert with identical chiffon-type gel can be achieved by mixing gelatin, LBG, soy protein, sugar and organic acid. (Mancuso and Common, 1960) In mayonnaises with oil content of less than ~ 60 %, rheological properties can be modified by replacing the oil with chemically modified starch and incorporating a stabilizer such as galactomannans (guar with small addition of LBG) and xanthan to the recipe.

Guar gum is used in barbecue and meat sauces, and in various salad dressing, to prevent phase separation and impact a desirable mouthfeel. Galactomannans are also added

to ketchups and dressing to increase viscosity and eliminate syneresis. In sterilized soups and sauces, galactomannans are used as thickeners in combination with xanthan at concentrations of ~0.2-0.5 %. In deep-frozen foods, the addition of cold solution galactomanan improves the freeze-thaw resistance, presumably by sterically hindering the formation of aggregates in the interstitial fluid phase. Other applications are as ingredient in sausage (to prevent weeping), in pumped meat blends (as a suspending agent), in fish fillets (as a binder and gluten replacer), in low-calories jams and spreads and in baked goods (as bologna), LBG is added to improve comminution of ingredients, to improve yield through the binding of free water, to extrude mixtures easily and to prevent phase separation during cooking, smoking and storage. (Nussinovitch, 1997)

LBG can also be used to achieve desired baked textures. The addition of LBG to wheat flours results in a softer, tastier product with an extended shelf life. Staling is retarded, crumbliness is reduced, and the quantity of eggs for the manufacture of biscuits, rolls and cakes is decreased. (Herald, 1986) The strength and pliability of baked tortillas can be improved by adding a blend of carob and guar gums. In producing dry mixtures for baking, the addition of carob and guar gum at maximum concentration of 0.15 % improves both mixing and the resultant mix's characteristics. When guar gum is added to dry cake, muffin, biscuit and pizza-crust mixes, it imparts shorter batter mixing times, less crumbling of the finished products, improved ingredient mixing, reduced moisture loss during storage and the ability to freeze the finished products.

3.4 Xanthan gum

Xanthan gum is produced by biotechnological processes. The polymer, which is produced by bacteria *Xanthomonas campestris*, is classified under the name B-1459 (Jean *et al.*, 1961). It can completely and effectively replace other natural gums. Many other species of *Xanthomonas* have been reported to produce extra cellular polysaccharides and in general extra cellular polysaccharides are produced by many species of microorganisms. After their production, they do not form covalent bonds with the microorganism's cell walls, being secreted instead into the culture media (Wilkinson, 1958). Xanthan gum is produced in the USA, Europe and Japan. The favored production method is fermentation, because it does not depend on variable factors such as weather and a product of more consistent quality is obtained, the price of which is less sensitive to political or economic shifts. The gum is recognized as harmless food additive for, among other purposes, thickening, when its usage follows reasonable and practical manufacturing practices.

3.4.1 Process of Xanthan gum

To produce xanthan gum, pure cultures of *X. Campestris* are grown using submerged aerobic fermentation in a sterilized medium composed of carbohydrates, a nitrogen source, phosphates (potassium) and trace minerals, that has been pre-inoculated with the selected strain in pilot-scale fermenter (Figure 3.13) This is followed by incubation at 30°C for 3 days in an industrial-scale fermenter, then a thermal treatment to eliminate viable microorganisms. This culture is precipitated by isopropyl alcohol and the fibers are separated by centrifugation, dried, milled and sieved then packaged (Urlacher & Dalbe, 1992)

The resultant products include standard grades of xanthan with size of 80 mesh, a fine-mesh grade (difficult to disperse but rapidly hydrated) with a particle size of 200 mesh, granulated powder with improved dispersibility and a transparent xanthan powder for clear

solutions at low concentration. The gum powder includes a very low total bacterial count, because of the sterilization process (Urlacher & Dalbe, 1992).

Xanthan production is influenced by the type and initial concentration of carbon and nitrogen sources, as well as by phosphate and citric concentration. (de Vuyst and Vermeire, 1994) An optimal, industrially useful fermentation medium was devised for *X. campestris*. It consisted of glucose, sucrose or sirodex A as the sole carbon source, corn-steep liquor as a combined on nitrogen-phosphate source and additional phosphate and citrate depending on the application the xanthan is destined for. Xanthan yield of 16.2, 15.1 and 16.5 g/kg were obtained after 96 hours fermentation on glucose (2 %) and sirodex A (2.8 %), respectively. The addition of citrate caused an increase in the pyruvate content of xanthan, with concomitant decrease in viscosity.

Product: Xanthan

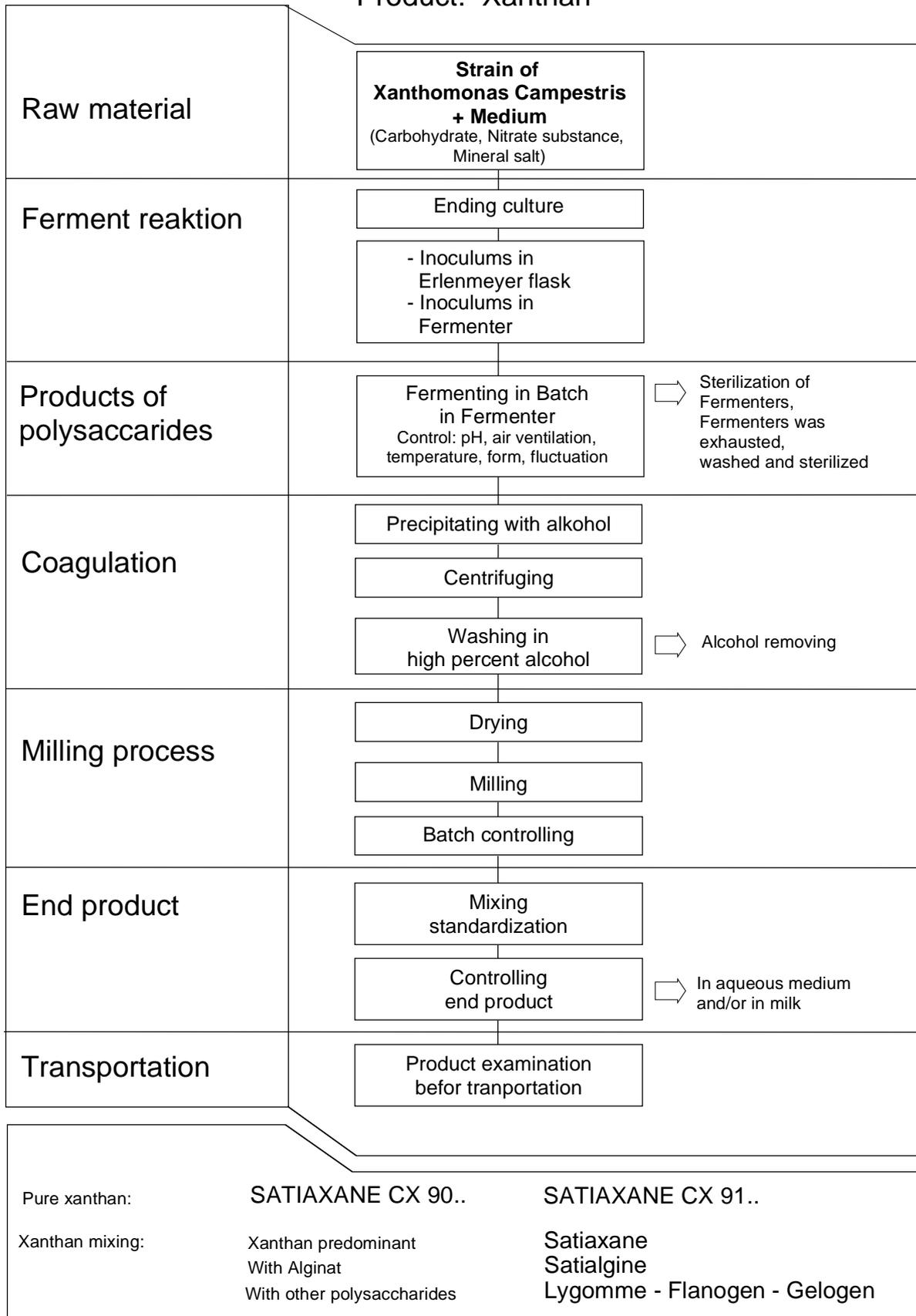


Figure 3.13 Xanthan production (Mero – Rousselot – Satia, 2000)

3.4.2 Structure

Xanthan gum is a microbial polysaccharide, composed of a 1-4-linked β -D-glucose backbone (like cellulose), with side-chains containing two mannose and one glucuronic acid (Figure 3.14). The pyruvic acid residues carried on half of the terminal mannose units represent $\sim 60\%$ of the molecule and give the gum many of its unique properties, e.g. its extraordinary resistance to hydrolysis and its uniform physical and chemical properties. (Melton *et al.*, 1976)

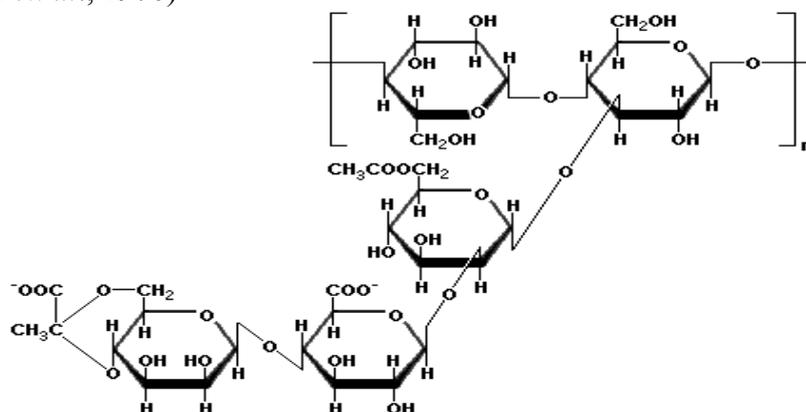


Figure 3.14 Structure of xanthan gum (Gibbons, 2002)

Xanthan has molecular weight of $\sim 2.5 \times 10^6$ with low polydispersity. Hydration in water is complete owing to its side-chains (Urlacher & Dalbe, 1992). Hydration rate ranges of xanthan gum were determined from its viscosity-time curves and used to study the effect of salt on gum-hydration rate (Kar Mun *et al.*, 1994). Xanthan's molecular conformation as determined by X-ray diffraction studies, consists of a helix (Figure 3.15) with a pitch of 4.7 nm and stabilization via hydrogen bonds (Moorhouse, 1992). It was proposed that, xanthan macromolecules in solution should be considered as single rigid helices, while or rejecting the existence of a double or triple helix. Under the influence of temperature, xanthan passes from a rigid ordered state to a more flexible disordered state. (Figure 3.16)

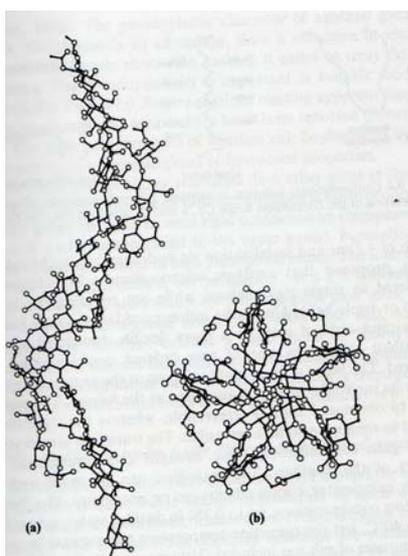


Figure 3.15 Helical conformation of xanthan gum viewed perpendicular (a) and parallel (b) to the helix axis. (Nussinovitch, 1997)

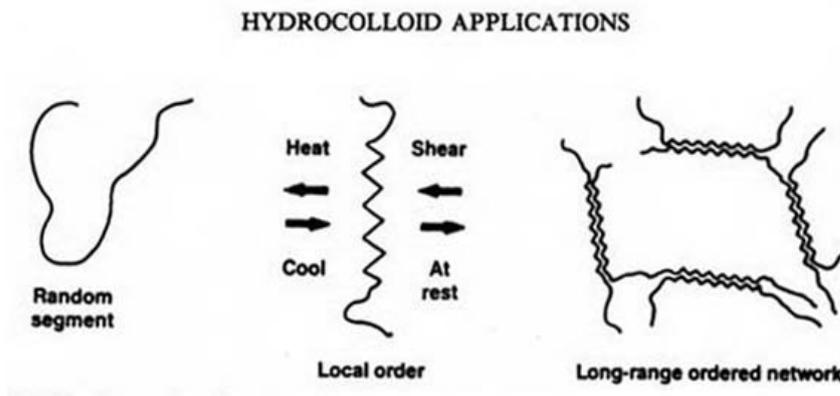


Figure 3.16 Conformational ordering in xanthan gum polysaccharides. (Nussinovitch, 1997)

3.4.3 Properties of xanthan gum

Commercial xanthan gum powder is a yellowish material, that is soluble in cold and hot water. The gum is easily dissolved in 8 % solutions of sulfuric, nitric and acetic acids, 10 % hydrochloric acid and 25 % phosphoric acid (Carnie, 1964). These solutions remain stable at room temperature for several months. Up to 50 % solvents, such as ethanol and propylene glycol, can be added to aqueous xanthan solutions and still be tolerated.

3.4.3.1 Viscosity

The viscosity of xanthan gum is function of its concentration is the dispersion. Viscosity versus xanthan gum concentration is comparable to other natural gums, such as guar gum and aliginite (Anon., 1960). The structure viscous behavior of xanthan gum solutions presents an advantage, since a reduction in viscosity values follows an increase in shear rate, making it easier to treat the food during processing. The structure viscous behavior is important in suitable food sensory qualities. (Kelco Co., 1975) The molecular structure of xanthan can be degraded by high shear rate, resulting in a decrease (loss) of functional properties. Xanthan solution promotes higher viscosities than other gums at the same low concentration. Shear-thinning of xanthan solution is more pronounced than with other gums owing to its semi-rigid conformation (compared with the random coil conformation found in the other gums). Formation of a weak network in solution results in high yield-point values.

3.4.3.2 Stability

Because of its secondary structure (side-chains wrapped around the cellulose backbone), xanthan is quite stable against degradation by acids or bases, heat treatments (high temperatures), freeze-thaw cycles, enzymes and long mixing. Xanthan solutions are stable over a wide range of pH, becoming affected only at pH value > 11 and < 2.5 . (Petit, 1982) At pH ~ 9 or above, xanthan gum gradually deacetylates. Its stability depends on gum concentration: the higher the concentration the more stable the solution. Gum solutions are degraded by high levels of strong oxidizing agents, such as persulfates, hypochlorite and hydrogen peroxide. Xanthan gums are compatible with high concentration of various salts. Xanthan has also been reported to exhibit iron-binding properties and antioxidative activity upon autoxidation of soy bean oil in emulsion (Shimada *et al.*, 1994).

In the range 10 - 90 °C, xanthan viscosity is almost unaffected in the presence of salts. After sterilization (30 min at 120 °C) of food products containing different gums,

only 10 % of viscosity is lost in products containing xanthan which is less than the loss seen with products containing other hydrocolloids, such as guar gum, alginate and CMC.

Stress-relaxation behavior of frozen 20 % sucrose solutions in the presence of 0.5 % xanthan gum, gelatin or guar gum was investigated using a thermomechanical analyzer. The calculated relaxation time and asymptotic modulus at temperatures within and above the glassy state were significantly affected by freezing rate and stabilizer identity. Xanthan and gelatin exerted the greatest effect. It is postulated that, above the critical concentration, stabilizer action may derive from a modification specifically altering the rheological and viscoelastic response of systems at subzero temperatures. (Sahagian and Goff, 1995)

3.4.3.3 Solution preparation

The preparation of xanthan solutions depends in their dispersibility and solubility. Dispersion occurs when the gum particles are introduced into liquid and separate from one another. Solubility is the process whereby particles swell and become viscous. Since the two processes are negatively related (easy dispersion means slow hydration), a suitable compromise needs to be found. Hydration depends on dispersion effectiveness, and the size of the gum particles relative to other ingredients in the mix. Lumping can be avoided by using a high-shear mixer and introducing the gum powder (previously mixed with other dry components of the mix if possible) through the top of the vortex. In commercial preparations, dispersion funnels or cyclone chambers are used to achieve rapid dispersion. (Urlacher & Dalbe, 1992) Rheological parameters was researched by Senge (2006)

3.4.4 Food Application

Xanthan is used as a stabilizer for dressing (oil-water emulsions). Ideally the product has high yield value (permitting the suspension of spices, herbs and vegetables and enabling the dressing to cling to the salad as well as to have body) and strong structure viscous behavior. These requirements make xanthan favorable for such an application. Product stability is not influenced by low pH (~ 3.5 in some dressing) and high salt (15 % or less), or thermal treatment. The uniform viscosity of xanthan from 5 to 70 °C also helps yield a uniform texture and good stability.

Xanthan gum can be used to control the rheological behavior of mayonnaise (Ma & Barbosa Canovas, 1995). Flow and viscoelastic properties at different oil and xanthan gum concentrations. (75 - 78 % and 0.5 - 1.5 %, respectively) were investigated using a plate-plate rheometer in rotational and oscillatory mode. Viscoelastic properties of mayonnaise were characterized using small-amplitude oscillatory shear, showing particle gel behavior.

Xanthan gum improves the mouthfeel of citrus and fruit-flavored beverages. In beverages that include flavor emulsions, the additive of xanthan at concentrations of up to 0.5 % can induced the stability and mouthfeel.

The use of xanthan in sauces, gravies, relishes, canned soups and dairy products has been previously described. Its heat stability and excellent stabilizing and suspension properties are important in canned foods. In whipped creams and mousses, the high yield values of xanthan were able to improve stabilizes air cells, and whipping is made easier by the gum's structure viscous behavior.

In instant mixes (drinks, soups and low-calories and desserts, instant milk shakes, sauces and breakfast drinks), xanthan is used as a thickener and a suspension and body agent at a concentration of about 0.1 - 0.2 % in such beverages, CMC-, or guar-xanthan gum blends are used.

Xanthan gum is also used to control the rheological properties of bakery products, such as rice cake. Turabi, Sumnu and Sahin (2008) have been used the different gums and gum blends (guar, carrageenan and xanthan gum) in order to replace gluten and improve stability properties. Rheological measurement was carried out by using the steady shear method, parallel-plate rheometer. All the formulations containing different kinds of gums with or without emulsifier blend showed shear thinning behavior, which means that apparent viscosity decreases as the shear rate increases. Rice cake containing guar and xanthan gums blends showed the highest viscosities, because of synergistic interaction. All gum except HPMC gum increased the emulsion stability of cake butter. Xanthan and emulsifier containing cake had the highest volume and porosity. Xanthan gum to the formulation increased the apparent viscosity of cake batter and prevented collapse of the cakes in the oven. Emulsifier blend addition resulted in soft cakes.

3.4.5 Xanthan interaction

Interactions between xanthan gum and other polysaccharides can have synergistic effects, such as enhanced viscosity or gelation with galactomannans and glucomannans. The synergistic interactions will all galactomannans, e.g. guar gum, locust bean gum and tara gum, can occur. Most importance is the guar and locust bean gum (LBG) interaction. LBG reacts more strongly, because its mannose to galactose ratio is 4:1 compared with 2:1 in guar gum. The interaction is suggested to occur between xanthan molecules and the 'smooth' regions of galactomannans, explaining the strong interaction with LBG, which is less branched than guar and has a more favorable galactose distribution. Xanthan gum also exhibits a definite reactivity with tara gum.

The xanthan-guar interaction leads to an increase in the solution's viscosity and elastic modulus. Such systems can be described by a measurement of the in-phase modulus G' (called elastic or storage modulus), and the out-of-phase modulus G'' (called viscous or loss modulus). $\tan \delta = G''/G'$ also provides information of the elasticity of such systems (a low value for $\tan \delta$ indicates an elastic network). Determinations of elastic modulus and apparent viscosity are important for the stabilization of emulsions or suspensions (e.g. salad dressing requires a high elastic modulus for stabilization, whereas in sauces and soups a high apparent viscosity is required while a high degree of elasticity is undesirable).

Maximum synergism in terms of viscosity (at several shear rate, 0.2 up to 21 s^{-1} can be achieved from blend with a total gum content of 1.0 %, of which xanthan makes up no more than 20 %. The synergism decreases in the presence of salts and is also influenced by gum concentration: the higher the latter, the greater the synergism. Xanthan-guar gum interactions are also important in cases in which blend ratios have lower elastic modulus values than xanthan gum alone, except with blends containing up to 30 % guar gum, which poses properties similar to those of pure xanthan and can, therefore, serve as valuable stabilizers.

The mechanisms of galactomannans-xanthan gum interaction have not exactly description. Many studies in the past have been investigated the mechanisms. Rock(1960) was the first report, who point out the synergistic interaction between xanthan and galactomannan. He reported that xanthan gum formed thermo-reversible gels with LBG but

not with guar gum. That can be described that lbg has fewer side chains than guar gum and, therefore, has a configuration that fits the xanthan molecule. McCleart *et al.* (1984) studied the interaction of xanthan gum with guar gum that had been treated with enzyme in order to provide samples with varying galactose contents. Although a mixture of xanthan (0.5 % w/v) and native guar (1.0 % w/v) with a galactose content of ~39 % did not gel following autoclaving at 120 °C and cooling to 20 °C, enzyme treated guar samples with galactose content decreased. When the galactose content was reduced further to 10 %, however, the sample has limited solubility, leading to a reduction in the values of these parameters.

3.5 Basic of Rheology

3.5.1 Definition

Rheology is the study of the deformation and flow behavior of mater. The science of rheology can be applied to any product and in fact was developed by scientist studying printing, inks, plastic, food and similar material. The food rheology is “the study of deformation and flow of the raw material, the intermediate products, and the final products of food industry” (Bourne, 2002) Rheology can be expressed in terms of viscous, elastic, and viscoelastic functions. In terms of fluid and solid phases, viscous functions are used to relate stress to shear rate in liquid systems, whereas elastic functions relate stress function to strain in solids. Viscoelastic properties cover materials that exhibit both viscous and elastic properties (Rao, 1999)

3.5.2 Viscosity

Movement of all fluids and liquid-like materials is based on the model of sliding of neighboring layers relative to each other when any external force applied to a body leads either to movement as a whole or to change in its initial shape (Malkin & Isayev, 2006). As shown in Figure 3.17, the lower plate is stationary and the upper plate is linearly displaced by an amount of dx when forces are applied (Tscheuschner, 2004; Malkin and Isayev, 2006). With a small deformation, the angle of shear is equal to shear strain, $\gamma = dx/dy$. Shear strain rate or shear rate, it can also be calculated as a velocity gradient established in a fluid as a result of an applied shear stress. It is expressed as $d\gamma/dt$ in a unit of 1/s. Shear stress is the stress component applied tangentially. It is equal to the force divided by the area of application and is expressed in units of force per unit area ($\sigma = F/A$ or τ) in Pascal (Pa) (Rao, 1999).

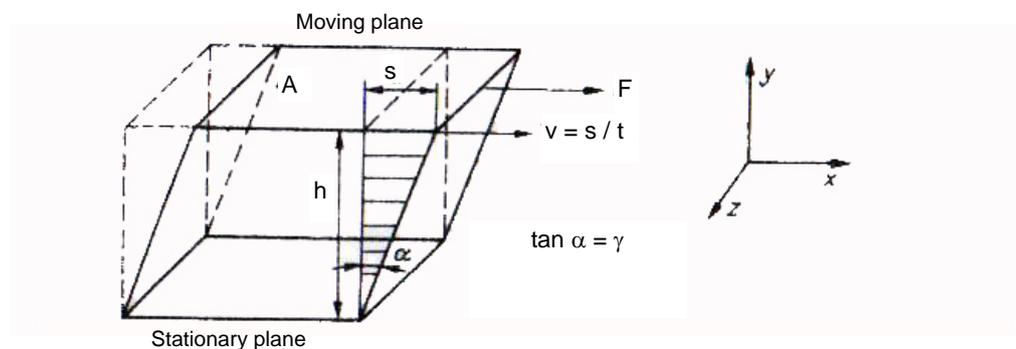


Fig. 3.17 Shear deformation of viscous body (modified from Tscheuschner, 2004)

Viscosity is the internal friction of a fluid or its tendency to resist flow. It is noted by the symbol η for Newtonian fluids whose viscosity does not depend on shear rate. It is defined as the proportional between shear stress and shear rate in units of Pas (Eq. 3.1)

$$\tau = \eta \cdot \dot{\gamma} = \eta \cdot \frac{dv}{dr} = \eta \frac{dv}{dh} = \frac{F_s}{A} ; \text{ for Newtonian fluids} \quad (\text{Eq. 3.1})$$

For non-Newtonian fluids, the relationship between shear stress and shear rate is non-linear. It shows the shear dependent with destruction of structure where the viscosity is not constant throughout a given shear rate. The viscosity can be so called functional viscosity, $\eta(\dot{\gamma})$. This functional viscosity can be defined as apparent viscosity η_{app} , or effective viscosity η_{eff} (Tscheuschner, 2004) and is dependent on shear rate. Fluidity ϕ of any material can be defined as $1/\eta$ in unit $1/\text{Pas}$. The effect of absolute temperature (T^*) on effective viscosity can be calculated by Frenkel-Eyring equation (Eq. 3.2).

$$\eta_{eff}(T^*, \dot{\gamma}) = A^* \left[\exp\left(\frac{E_A}{\mathfrak{R}T^*}\right) \right] \quad \text{in Pa}\cdot\text{s} \quad (\text{Eq. 3.2})$$

3.6.2 Fluid flow behavior

The major types of fluid flow behavior can be described by means of function between shear rate and shear stress as shown in Table 3.8. From Table 3.8, by fitting the regression parameters in these given equations, the effective or apparent viscosities can be calculated in the dependent on shear rate. The fluid that is independent on shear rate can be explained by Newton's equation. Ostwald-de Waele was used for the group of non-Newtonian fluids for more than 95 % of cases. On the contrary, the assumptions of Bingham-, Casson- and Herschel-Bulkley equations were used for the non-Newtonian materials (solid-like behavior). The parameters in these equations can be used to describe the structure degradation and also the flow behavior changing in processing. The appropriate equations were selected according to the number of parameters and the successful regression of flow curves. The less number of parameters and the high correlation between experimental data and model equation, i.e., the high correlation coefficient (r) and standard deviation (SD), would be the criteria of selections.

Table 3.8 Standard rheological models with defined viscosity

Model	Equation	Effective viscosity	Number of model parameters
	$\tau = f(\dot{\gamma})$ in Pa	$\eta_{eff} = f(\dot{\gamma})$ in Pas	
Newton	$\tau = \eta \cdot \dot{\gamma}^1$ (3.3)	$\eta_{dyn} \neq f(\dot{\gamma})$	1
Ostwald-de Waele	$\tau = K \cdot \dot{\gamma}^n$ (3.4)	$\eta_{eff} = f(\dot{\gamma}) = K \cdot \dot{\gamma}^{n-1}$ (3.5)	2
		$\eta_{proz} = f(\dot{\gamma}) = n \cdot K \cdot \dot{\gamma}^{n-1}$ (3.6)	2
Herschel-Bulkley	$\tau = \tau_0 + K \cdot \dot{\gamma}^n$ (3.7)	$\eta_{eff} = \frac{\tau_0}{\dot{\gamma}} + K \cdot \dot{\gamma}^{n-1}$ (3.8)	3 Non-linear plastic
Bingham	$\tau = \tau_0 + \eta_{BH} \cdot \dot{\gamma}$ (3.9)	$\eta_{eff} = \frac{\tau_0}{\dot{\gamma}} + \eta_{BH}$ (3.10)	2 Linear plastic
Casson	$\tau = \sqrt{\tau_0} + \sqrt{\eta_{CA} \cdot \dot{\gamma}}$ (3.11)	$\eta_{eff} = \frac{\tau_0}{\dot{\gamma}} + \eta_{CA} + 2\sqrt{\tau_{0CA} \cdot \eta_{CA} / \dot{\gamma}}$ (3.12)	2 Non-linear plastic

3.5.3 Yield stress

This yield point (τ_0) parameter refers to the material that exhibits semi-solid with particle micro-gel dispersion. This parameter is the criteria of the energy input of the mechanical forces in process. It describes the structural characteristic of the dispersion phase and the viscosity in each model as follows.

$\tau < \tau_0$	elastic behavior
$\tau = \tau_0$	solid-liquid transition
$\tau > \tau_0$	viscous behavior

3.5.4 Viscoelasticity

All material has viscoelastic properties. Viscoelasticity of materials represents simultaneously the properties of reversible elastic behavior and irreversible viscous behavior. Viscoelastic behavior of many foods can be determined by means of oscillatory testing. Small amplitude oscillatory shear, also called dynamic rheological experiment, can be used (Rao, 1999). In the small amplitude oscillatory shear experiment, a sinusoidal oscillating stress or strain with a frequency f is applied to the material, and the phase different between the oscillating stress and strain, as well as the amplitude ratio, is measured. The information obtained should be equivalent to data from a transient experiment at time; $t = f^{-1}$ (Rao, 1999).

In an oscillatory test a food sample is subjected to a small sinusoidal oscillating strain or deformation $\gamma(t)$ at time t according to Eq. 3.13 for evaluating the elastic component. Differentiation yields the next equation of Eq. 3.14, which shows the strain rate $\dot{\gamma}(t)$ for evaluating the viscous component to be $-\pi/2$ radians out of phase with the strain.

$$\tau = G \cdot \gamma + \eta \cdot \dot{\gamma} \quad \text{in Pa} \quad ; \text{ dominant in elastic component} \quad (\text{Eq. 3.13})$$

$$\dot{\gamma} = \frac{\tau}{G} + \frac{\eta}{\dot{\gamma}} \quad \text{in 1/s} \quad ; \text{ dominant in viscous component} \quad (\text{Eq. 3.14})$$

The applied strain generates two stress components in the viscoelastic material. First is an elastic component in line with the strain (stress and strain are in phase), the second is a viscous component, -90° out of phase (stress and strain are $-\pi/2$ radians out of phase) as shown in appendix A.

For deformation within the linear viscoelastic range, the generated stress σ_0 can be expressed in terms of an elastic or storage modulus G' (Eq. 3.15), a viscous or loss modulus G'' (Eq. 3.16) and loss factor $\tan \delta$ (Eq. 3.17), as shown in the following equations.

$$G' = \frac{\sigma_0}{\gamma_0} \cos \delta \quad \text{in Pa} \quad (\text{Eq. 3.15})$$

$$G'' = \frac{\sigma_0}{\gamma_0} \sin \delta \quad \text{in Pa} \quad (\text{Eq. 3.16})$$

$$\tan \delta = \frac{G''}{G'} \quad (\text{Eq. 3.17})$$

$$|G^*| = \sqrt{(G')^2 + (G'')^2} \quad \text{in Pa} \quad (\text{Eq. 3.18})$$

$$|\eta^*| = \sqrt{(\eta')^2 + (\eta'')^2} \quad \text{in Pas} \quad (\text{Eq. 3.19})$$

The storage modulus G' expresses the magnitude of the energy that is stored in the material or recoverable per cycle of deformation. G'' is a measure of the energy that is lost as viscous dissipation per cycle of deformation. It is noted that if G' is much greater than G'' the material will behave as solid-like or elastic. If the G'' is much greater than G' the material will behave as liquid-like.

The dynamic oscillation tests can be used to obtain useful properties of viscoelastic foods as described as follows.

Amplitude sweeps: This study is to determine G' and G'' as a function of amplitude at a fixed frequency and temperature (in appendix A). The linear curve in a small oscillating regime expresses the microstructure of material which has no structural change within the studied range.

Frequency sweeps: This study is to determine G' and G'' as a function of frequency (f) at a fixed amplitude, especially in the linear regime, and temperature (in appendix A). Based on frequency sweeps, one can designate solid-like and liquid-like properties. For example, for dilute biopolymer solution, G'' is usually larger than G' which presents a liquid-like behavior. For concentrated biopolymer solution, G' is usually larger than G'' which presents a solid-like behavior.

Temperature sweep: This study is to determine G' and G'' as a function of temperature at fixed ω . This test is well suited for studying gel formation during cooling of a heated dispersion during heating and gel formation of proteins.

3.6 Basic of rheology for semi-solid food

Rheology is broadly determined as the study of the determination and flow of the material. "Rheology" term is usually referred to non-Newtonian material of which polymeric material are the most importance class, in an economic. Characteristic of the rheological behavior of materials from their shear rate and shear stress relationship was called "Flow curve" and quantitative understanding of their behavior is useful in material handling and process design.

Semi-solid foods, which are ketchup or fruit puree, is the one of importance commercial products in many countries, such as South-East Asia countries, South Africa. The most of semi-solid foods perform the shear thinning behavior. Fruit product basically contains sugar content and some thickener content. The juice contains sugar content which plays a major role in the magnitude of viscosity and the effect of temperature on viscosity. Rheological behavior of concentrated puree can be found in studies on the non food dispersion. The system of particles flow is may be called a kinetic or structural approach to rheology of suspensions, where the basic flow units are assumed to be small clusters, or aggregates, that at low shear rates give the suspension a finite yield stress.

3.6.1 Structure examination of potato puree infant food

Infant food is one of importance example for semi-solid food and carried out around the world recently, particularly in the Unites State, which are most of it utilized to manufacture baby food. The product has advantage as infant food over other cereal based baby foods, especially wheat and wheat related to cereals, due to its hypoallergenic effect (Maleki, 2001). Baby food manufacture has recommended that infant food should be served warm before feed and consumed quickly. Any left over feed should be properly refrigerated if intended to be consumed within 72 hours. Rheological properties have been considered to be analyzed tool for investigating the infant food properties and structural organization of infant food. Admed and Ramaswamy (2006) studied structure of potato infant food on temperature effect. Infant food showed the weak gel formation, because G' was higher than G'' and the magnitudes of both parameters increase with frequency. (Figure 18) Moreover, This can be implied that elastic modulus was relatively independent of frequency while the viscous modulus was dependent on frequency.

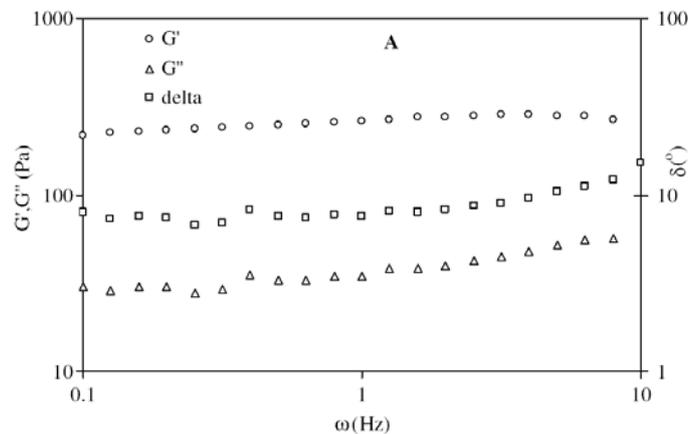


Figure 3.18 Dependence of elastic G' , viscous G'' moduli, and phase angle, δ for sweet potato puree based baby food

Steady shear rate was used to investigate the effect of temperature in infant food. Result showed that potato puree based on baby food performed the non-Newtonian shear-thinning behavior ($n < 1$) with temperature. (Figure 19) Sweet potato starch has a fairly high peak and initial hot paste viscosity (commonly found between 58 and 80 °C), thinning rapidly on prolonged cooking at boiling temperature. (Raspas, 1969)

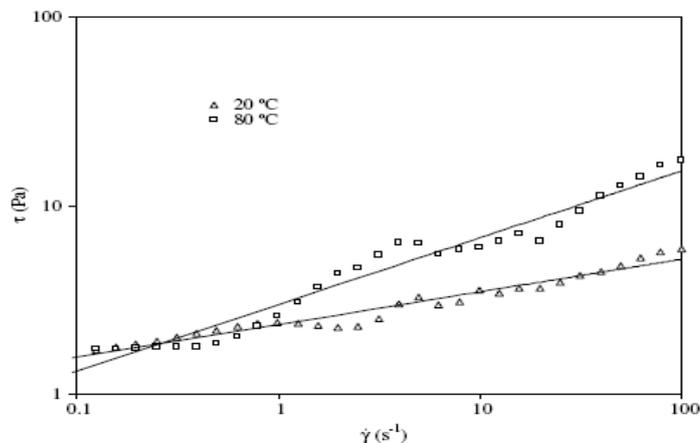


Figure 3.19 Shear stress-shear rate data of sweet potato puree based baby food at selected temperature

3.6.2 Rheological properties of fruit purees

The rheology properties of fruit and vegetables are of interest to plant physiologists, horticulturalists, agricultural engineers and food engineers due to different causes. Fruit, fruits and vegetables are increasing in importance in the contemporary human diet. Secondly, the rheological properties are relevant to several aspects of the study of these materials, including the causes and extent of damage during harvesting, transport and storage; the human perception of product quality; and the physiological changes that take place in the product during growth, maturation, ripening and storage after harvest. (Rao and Steffe, 1992) In general, puree of fruits and vegetables are structure fluids behavior (Rao, 1977) Maceiras, Alvarez and Cancela (2006) investigated the rheological properties of different fruit puree (raspberry, strawberry, peach and prune). Diagram between apparent viscosity (η) against shear rate (γ) (Figure 20 and 21) showed that the variation is exponential and therefore they are non-Newtonian fluid.

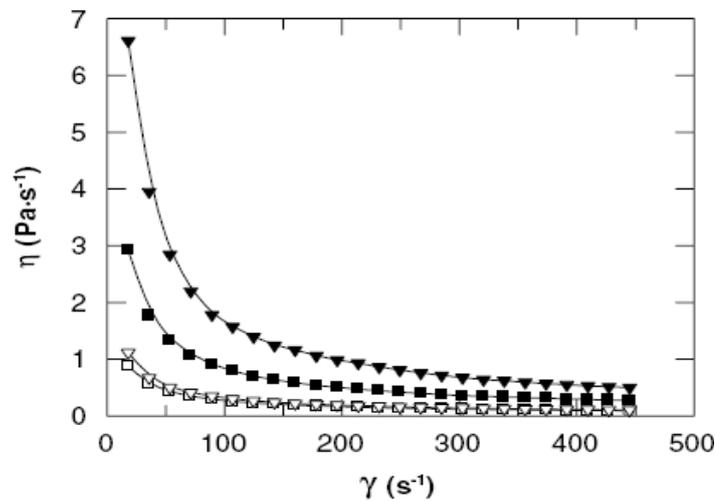


Figure 3.20 Viscosity vs. shear rate for different fruit purees at 20 °C: prune jam (\blacktriangledown), raspberry jam (\blacksquare), prune puree (\triangledown) and raspberry puree (\square)

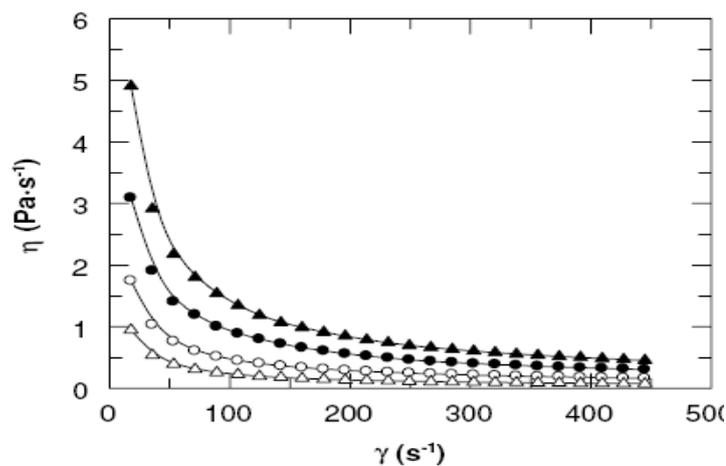


Figure 3.21 Viscosity depend on shear rate for different fruit purees at 20 °C: strawberry jam (\blacktriangle), peach jam (\bullet), peach puree (\circ) and strawberry puree (Δ)

3.6.3 Model for describing flow behavior of semi-solid foods

A flow model is considered to be the mathematical equation that can describe rheological data, such as shear rate-shear stress data in basic shear diagram, and it provides a

convenient and concise manner of describing the data. Occasionally, such as for the viscosity versus temperature data during starch gelatinization, more than one equation may be necessary to describe the rheological properties. The difference type of food was used the different model to describe the behavior. The factor have also affected with rheological properties, such as temperature, concentration, so it might be used the different model for describing, even which the same type of food. Most of semi-solid food perform the shear thinning behavior and yield stress. Therefore, the model which always uses to describe the behavior is Herschel-Bulkley Model. (Eq. 3.20) This equation is useful, when yield stress of food is measurable.

$$\tau = \tau_0 + K \dot{\gamma}^n \quad (\text{Eq. 3.20})$$

Where is τ_0 yield point (Pa), τ is shear stress (Pa), K is the consistency index (Pasⁿ), n is the flow index and $\dot{\gamma}$ is the shear rate (s⁻¹). The concept of yield stress has been Bernes and Walters, (1985), because a fluid may deform minutely at stress values lower than the yield stress. Nevertheless, yield stress may be considered to be engineering realities that play an importance role in food products. However, some case of semisolid foods don't show the yield stress value or show the negative value, Herschel-Bulkley model is not able to describe those food. Flow behavior of those can be described by Ostwald-de Waele model. (Eq. 3.21)

$$\tau = K \dot{\gamma}^n \quad (\text{Eq. 3.21})$$

Where K , the consistency index (Pasⁿ), is the shear stress at shear rate of 1.0 s⁻¹ and the exponent n , the flow behavior index, is dimensionless that also reflects the closeness to Newtonian flow. For the special case of a Newtonian fluid ($n = 1$). When magititude of $n < 1$ the fluid is shear-thinning, and when $n > 1$ the fluid is shear- thickening in nature. As stability term, flow index can determine the structure organization. When flow index value was near 0, stability is high.

Ahmad and Ramaswamy (2005) described the rheological properties of potato puree based on infant food product by Herschel-Bulkley model. The yield stress of potato puree was between 0.54 to 1.70 Pa and flow index (n) was less than. Thus, potato puree showed non-Newtonian shear-thinning behavior.

Maceiras, Alvarez and Cannela (2006) investigated the effect of cooking on rheological properties of fruit puree. The flow behavior was analyzed by two different rheological models; Ostwald de-Walle model and Herschel-Bulkley model. The result showed that both of models fitted reasonably well the examine data at all temperature ($r > 0.988$).

Wei , Wang and Wu (2001) studied the flow properties of fruit filling by using model, which make from waxy corn starch, fructose, citrate buffer and guar (guar gum, locust bean gum, CMC, xanthan gum or K-carrageenan. The rheolgical parameter was fitted in Herschel-Bulkley equation for structure fluids behavior. Adding guar gum, locust bean gum and CMC increased the modeified consistency index and consequently the power term, while adding xanthan gum and L-carrageenan decreased them.

Chapter 4 Material and Methods

4.1 Materials

4.1.1 Material of pineapple puree

Pineapples fruit (*Ananas comosus* L.) Red Spanish, which exported from Ivory Coast, were obtained from local market in Berlin. Fruits were stored at refrigerator ($5 \pm 1^\circ\text{C}$) and 80 % relative humidity until puree preparation. Pineapple was able to classify by color of skin and meat, texture and country of produce. Texture and color of pineapple was determined by appearance measurement. Xanthan gum, guar gum and locust bean gum were supported by Lolyma GmbH, Germany. Pectin was supported by Herbstreith & Fox, Germany.

4.1.2 Material of selected commercial fruit puree for compared with pineapple puree product

The commercial puree products 8 kind of fruit puree and 4 different bands were purchased from local supermarket (LIDL, Reichert) and health shop (Rossmann) in Berlin, Germany. (Table 4.1) Six of them were consumed as baby food. And two of them were consumed as desert. The products were tested soon after their container opened.

Table 4.1 Source of commercial samples

Type of puree	Consume	Source	Band
Apple mus	Dessert	Reichert Supermarket	Diatini
Apple mus	Dessert	Reichert Supermarlet	Odenwald
Banana in apple puree	Baby food	EDEKA supermarket	Bebivitta
Banana in apple puree	Baby food	Rossmann store	HiPP
Peace in maracuja	Baby food	EDEKA supermarket	Bebivita
Peace in apple	Baby food	Rossmann store	HiPP
Pear puree	Baby food	EDEKA supermarket	Bebivita
Fruit salad	Baby food	Reichert supermarket	HiPP

The commercial products were investigated on rheological properties, using shear examination (CSR), oscillation tests (Frequency sweep, Amplitude sweep and temperature sweep).

4.2 Method

4.2.1 Preparation of pineapple fruits

The important factor for pineapple examination was the ripening. The characteristic of pineapple at different level of ripening was Pineapple was investigated the level of ripening by using the texture analyzer and color measurement. During storing sample, pineapple was kept in refrigerator ($5 \pm 1\text{ K}$). A sample was picked every 2 days until skin of pineapple changed to dark yellow. The importance indicator to study the pineapple characteristics on each level of ripening was texture properties of meat, color of pineapple skin, color of pineapple meat, soluble solid and pH.

Fresh pineapple was stored in refrigerator (5°C) until the color of skin of half fruit change to yellow. Basically, color of pineapple skin was suitable non-destructive indicator to determine the level of maturity of pineapple. During storage, pineapple was changed from green to yellow, which started from bottom (opposite to the crown of pineapple). The suitable level of ripening (according to pineapple's ripening examination), color of pineapple peel was turn to yellow on half fruit.

4.2.2 Pineapple puree process

Process of pineapple puree preparation was started with slice the pineapple into 1 cm thick and used the two sizes of ring to remove the skin and core from pineapple meat and washed in

water. Pineapple meat was cut to 1 cm³. Pineapple was blended in the kitchen blender for 3 min at speed number 3. Pineapple puree was removed a fiber by using sieve. (Diameter 2 mm) Last step, puree was packed in the plastic bag (1 kg per bag) and freeze in the freezer (-17 °C) until using.

4.2.3 Hydrocolloid preparation

Gums was investigated the rheological properties before added to the pineapple puree. In this studied was emphasized on a stability properties of each gums, which of pectin, gaur gum, xanthan gum, and locust bean gum.

4.2.3.1 Pectin solution preparation

The types of pectin were divided into 2 groups, such as citrus pectin and apple pectin. Each group of pectin have a 3 different level of DE value such as low DE (less than 10 %), high DE(around 50 %) and high DE (Higher than 70 %). Pectin solution was prepared in distilled water at room temperature. A solution was blending in speed of 600 rpm. The solution of pectin was stored in refrigerator (5 °C) overnight.

Pectin has a reaction with sugar to dispersion, so this experiment also did the mixing pectin and sugar. To study an effect of sugar on pectin, a ratio of pectin, sugar and water was followed by 2:10:88, 2:20:78, 2:30:68, 2:40:58 and 2:50:48.

4.2.3.2 Xanthan solution preparation

Xanthan solution was prepared in distilled water at normal temperature. The level of concentration was prepared at 5 levels of percents which 0.2, 0.4, 0.6, 0.8 and 1%. Before adding xanthan gum, pineapple puree was stir at 2 min in order to pre-homogenize the structure of puree. After that, xanthan gum was applied to puree slowly until finish. Stirring was continuing for 10 minutes. It stored over night in refrigerator (5 °C). Before test, the sample was put in normal temperature in order to adjust the temperature of solution.

4.2.3.3 Guar gum solution preparation

The preparation of guar gum solution has been carried out the same method as xanthan gum preparation methods. Guar gum solution was prepared for 5 level of concentration which 0.2, 0.4, 0.6, 0.8 and 1 %.

4.2.3.4 Mixed gum solution preparation

To study the interaction between gums, the interaction between galactomannan and xanthan gum was considered to be high effect of synergistic, so this experiment emphasized the interaction of galactomannan and xanthan gum. Some selected galactomannan was chosen investigated the effect of interaction which was locust bean gum and guar gum. The study was divided into two groups by changed a kind of galactomannan. First group was a interaction between guar gum and xanthan gum. And another group was interaction between locust bean gum and xanthan gum. (Figure 4.7)

4.2.3.4.1 Guar and xanthan gum mixed solution preparation

The preparation of guar gum and xanthan gum solution started with guar gum powder and xanthan gum powder mixing in a beaker and stirred for 1 minute. After that, the mixing powder was dissolved in distilled water and stirred by stirrer for 10 minutes at 600 rpm. The guar and xanthan gum solution was stored over night in refrigerator (5 °C). To study the interaction of guar and xanthan gum, the ratio between guar and xanthan gum was considered to be the importance factor for effect of rheology properties. The ratio between guar gum and xanthan gum for study was 0:100, 15:85, 25:75, 50:50, 75:25, 85:15 and 100:0.

4.2.3.4.2 Locust bean gum and xanthan gum solution preparation

The preparation of locust bean gum and xanthan gum began by mixed locust bean gum powder and xanthan gum powder. After that, the powder mixing was dissolved in distilled water in the 100 ml of beaker and stirred for 10 minutes at 600 rpm. The gum mixing solution was heat for 5 minute at temperature of 75 °C. After heating, the solution was cooled down in room temperature for 1 hour. The mixed gum solution was stored over night in refrigerator before tested. The ratio factor was varied in this experiment, which 0:100, 15:85, 25:75, 50:50, 75:25, 85:15 and 100:0.

4.2.4 Preparation of pineapple puree with stabilizer

4.2.4.1 Preparation of pineapple puree with pectin

The preparation of pineapple puree mixed gum began by thawed the freezing pineapple for 4 hours. Before mixed with gum, pineapple puree was stirred by stirrer for 1 minute at 600 rpm in order to pre-homogenize the puree. For the reason, pineapple puree after freezing separated into 2 phases, which was juice and form, because of freeze-thaw effect. The gums powder was applied in pineapple puree slowly during stirred at 600 rpm. After applied all the gums, pineapple puree mixed gums was continue stirred for 10 minutes at 600 rpm. In case of pineapple puree mixed pectin, pectin mixed with sugar in the beaker before applied to pineapple puree. After mixed gums in pineapple puree, the samples was stored over night in refrigerator. (5 °C)

4.2.4.2 Effect of type of pectin on pineapple puree

The different type and different level DE of pectin was added in pineapple puree. Pectin was divided into 2 groups, which made from citrus peel (CU) and apple peel (AU). Each type of pectin was also able to classify by the level of DE (Degree of esterification) for three groups that was high level of DE (More than 70), medium level of DE (around 50) and low level of DE (less than 10). (Table 4.2)

Table 4.2 Type of pectin samples

Number	Code	Source	DE
1	AU 910	Apple	4.3
2	AU 607	Apple	51.1
3	AU L063/05	Apple	35.7
4	AU 202	Apple	68.4
5	CU 902	Citrus	9.6
6	CU 701	Citrus	35.1
7	CU L063/05	Citrus	49.9
8	CU 201	Citrus	70.1

4.2.4.3 Effect of sugar on pineapple puree with pectin

Pineapple puree, which was after thawing for 24 hr, was pre-mixed by stir with stirrer for 2 min at speed of 400 rpm, as pineapple particle mixing purpose. For puree and pectin combination, sugar was one of importance factor, because sugar plays the role of dispersion assistance and enhances the viscosity of pectin and pineapple puree. So, sugar was considered to be the importance factor in pectin and puree combination. Sugar was added in pineapple puree that varied follow a percent of sugar concentration. It was from 10, 20, 30 40, 50, 60 percent of sugar concentration.

4.2.4.4 Effect of concentration of Calcium and concentration of pectin

Calcium was added in pineapple puree together with pectin, on purpose to induce viscosity of pectin. Calcium was related factor with concentration of pectin. To study the relationship

between among of calcium and concentration of pectin, pineapple puree added the calcium, which 0.2, 0.4, 0.6, 0.8 and 1 % of concentration. For concentration of pectin, pectin was added to puree about 1, 2, 3 percent of concentration.

4.2.4.5 Effect of guar gum on pineapple puree

Pineapple puree was prepared the same method of previous examination, which thawed, stirred and measured pH. Guar gum was added to pineapple puree slowly during stirred by stirrer at 600 rpm. After that, pineapple purees mixed guar gum continue stirred for 10 min at 600 rpm. Before tested rheological examination, sample stored over night in refrigerator. To investigate the effect of guar gum to stabilize the structure of pineapple puree, the concentration of guar gum was the suitable factor to use in this experiment. Guar gum was added to puree in different concentration that was 0.2, 0.4, 0.6, 0.8 and 1 percent.

4.2.4.6 Effect of locust bean gum on pineapple puree

The preparation of pineapple puree used the same method of previous examination that thawed, stirred and measured pH. Guar gum was added to pineapple puree slowly during stirred for 600 rpm. However, locust bean gum would show good performance, when dissolve in hot water or heating after dissolve in water or puree. After added guar gum in puree, puree was heated in water bath at temperature of 70 °C and stirred together at 300 rpm for 15 minutes. Sample was cooled down at room temperature for 1 hour and stored in refrigerator over night. Locust bean gum was added to puree in different concentration that was 0.2, 0.4, 0.6, 0.8 and 1 percent.

4.2.4.7 Effect of xanthan on pineapple puree

Preparation of pineapple puree added xanthan gums started the same as pineapple puree added guar preparation method which thawed for 4 hours and stirred for 2 minute. Xanthan gum was added to puree in different concentration, which was 0.2, 0.4, 0.6, 0.8 and 1 percent.

4.2.4.8 Effect of interaction between galactomannan and xanthan gum on pineapple puree

Preparation of pineapple puree mixed with mixing gums started with mixed the galactomannan powder (Locust bean gum or guar gum) and xanthan gum together in 100 ml beaker. Before added gums in pineapple puree, freezing pineapple puree was thawed in room temperature for 4 hours and stirred by stirred for 2 min at 600 rpm. Mixing gums powder was added slowly in pineapple puree during stirred at 600 rpm until finish among of powder. The pineapple puree added with mixing gum stored in refrigerator for overnight. To study the synergistic system of mixed gum in pineapple puree, pineapple puree added gum mixing was investigated the rheological properties, such as steady shear rate examination and oscillation test.

4.2.4.8.1 Interaction between guar gum and xanthan gum on pineapple puree

Pineapple puree was prepared the same as previous examination. Before mixed guar gum and xanthan gum in pineapple puree, the both gums powder was mixed in beaker and stirred for 1 minute. After that, it was added to pineapple puree slowly during stirred. After finish adding, pineapple puree added gums were continually stirred for 10 minute at 600 rpm. Sample was stored overnight in refrigerator (5 °C) The concentration of gums was calculated in ratio between Guar gum and xanthan gum which 0:100, 15:85, 25:75, 50:50, 75:25, 85:15 and 100:0.

4.2.4.8.2 Interaction between locust bean gum and xanthan gum on pineapple puree

Pineapple puree was prepared the same as previous examination. The preparation of gums also the same as examination of guar gum and xanthan gum which mixed the gums powder at first. After that, it dissolved in puree. For pineapple puree added locust bean gum and xanthan gum, the

puree added mixed gum was heated at 70 °C and cooled down at room temperature for 1 hour before stored overnight in room temperature. A ratio of locust bean gum and xanthan was added to puree that was 0:100, 15:85, 25:75, 50:50, 75:25, 85:15 and 100:0.

4.3 Method of material science examination

4.3.1 Method of rheological examinations:

All of rheological measurements were used Rotational measurements and Oscillatory measurements. The measurements have been performed on a Physica UDS 200 Rheometer (Figure 4.1) equipped with an electronically commutated synchronous motor allowing rheological testing in controlled stress and strain modes. The instrument allows the individual creation of complex real time tests contain large number of different intervals in controlled stress and control stain, both in rotational and oscillatory modes. The direct strain oscillation option based on a real position control as described above has been used for oscillatory testing. Precise temperature control was managed by Peltier Cylinder temperature system TEZ 150 that assures minimal temperature gradient across the measuring the gap by patent protection design, (± 0.01 K)



Figure 4.1 Physica UDS 200 rheometer

4.3.1.1. Shear rate examination

4.3.1.1.1 Rheological method for gums solution analysis

The rheological measurement for gum solution analyze has been carried out on a Physica UDS 200, equipped with an electronically commutated synchronous motor allowing rheological testing in controlled stress and control stain mode. The measurement system used Double Gap head model DG 26.7. (Figure 4.2) And the measurement method used the one phase by measured from 1000 s^{-1} to 0 s^{-1} of shear rate. ($\dot{\gamma}$) (Total point is 20 point).



Figure 4.2 Double gap head set model DG 26.7

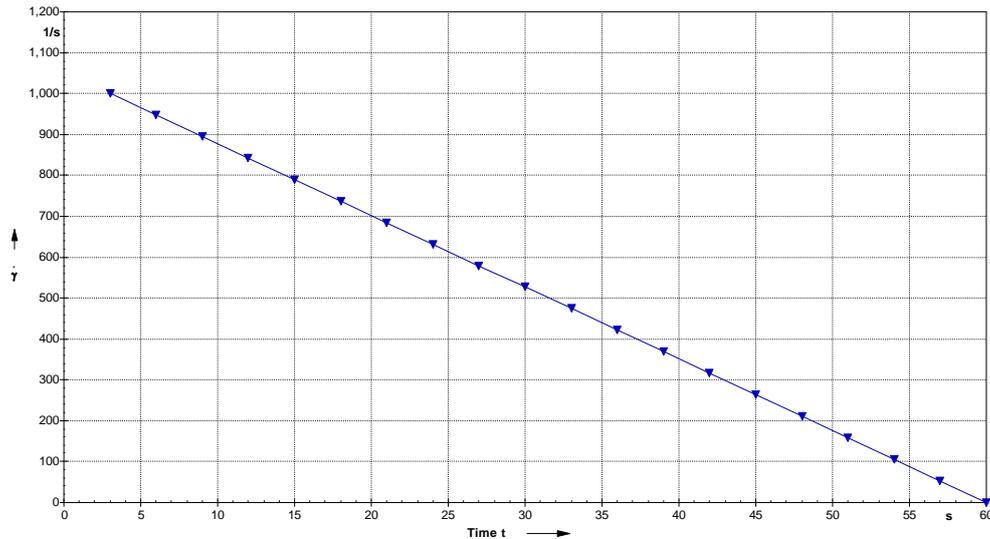


Figure 4.3 Measurement phase for gums solution

4.3.1.1.2 Rheological method for puree product analysis

The rotational measurement was analyzed by UDS 200 rheometer, measurement system: Z3 DIN and Peltier Cylinder temperature system TEZ 150P. The measurement condition was used the shear rate up to 50 s^{-1} . The measurements were made on 5 phase (Figure 4.13) :

- Phase 1: Phase duration 1 min (20 measurement points, measuring point duration 3 s)
Shear rate ($\dot{\gamma}$) = $50/\text{s}$ constant
- Phase 2: Phase duration 1 min (20 measurement points, measuring point duration 1 min)
Shear rate ($\dot{\gamma}$) = $0/\text{s}$ constant
- Phase 3: Phase duration 1 min (20 measurement points, measuring point duration 3 s)
Shear rate ($\dot{\gamma}$) = $0.1 \dots \dots 50/\text{s}$ with time
- Phase 4 : Phase duration 1 min (20 measurement points, measuring point duration 3 s)
Shear rate ($\dot{\gamma}$) = $50/\text{s}$ constant
- Phase 5: Phase duration 1 min (20 measurement points, measuring point duration 3 s)
Shear rate ($\dot{\gamma}$) = $50 \dots \dots 0.1/\text{s}$ with time

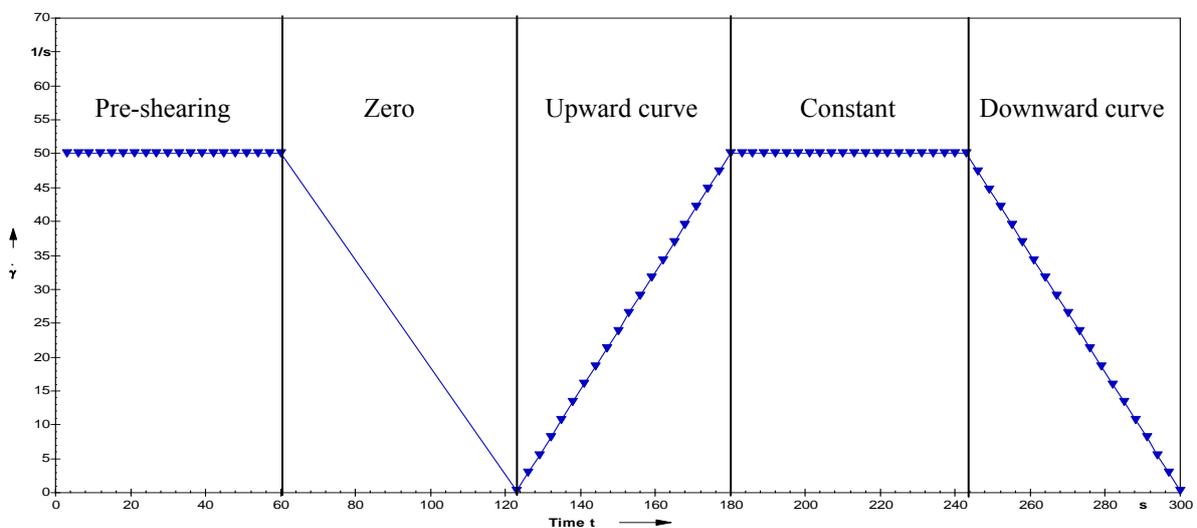


Figure 4.4 Five phase of complex measurement curve

4.3.1.2 Oscillation test

The oscillatory measurements made by UDS 200 rheometer, measurement system: Z3 DIN geriffely and Peltier Cylinder temperature system TEZ 150P. The type of oscillatory measurements were measured as frequency sweep and amplitude sweep at temperature (20, 30, 40, 50, 60 °C) for all sample under investigation.

Frequency sweep

The frequency sweep has done at constant strain rate of 0.001 in frequency range from 10 to 0.01 Hz. The data performed as storage modulus (G'), loss modulus (G'') and angular frequency ($\tan \delta$)

Amplitude sweep

The amplitude sweep was used one phase measurement. A condition of measurement was 30 points of measurement. Deformation amplitude $0.0001 \leq \gamma \leq 0.1$, angular frequency = 1 s^{-1}

Temperature sweep

The pineapple puree was determined the effect of temperature on its structure by using temperature sweep method. The structure of pineapple puree was analyzed at temperature of 20 °C to 60 °C.

4.3.1.3 Analysis of rheological measurement

4.3.1.3.1 Rotational measurement analysis:

The data analyzed by using Rheoplus 32 Multi 6 version 3.40. The Herschel-Bulkley and Ostwald-de Waele math models used to fit the curve and parameter of rheological measurement.

Herschel-Bulkley model:

This model describes the flow curve of material with yield stress and shear thinning or shear thickening behavior at stresses above the yield to calculate the viscosity and yield point fo ideal-viscous fluid.

$$\tau = \tau_0 + K \cdot \dot{\gamma}^n \quad (\text{Eq. 4.1})$$

Ostwald-de Waele Model

This model describes the flow behavior of material as same as Herchel-Bulkley model, but the calculation was not related with yield stress (τ_0)

$$\tau = K \cdot \dot{\gamma}^n \quad (\text{Eq. 4.2})$$

4.3.1.3.2 Oscillatory measurement analysis

The oscillatory date evaluated into 3 variables: storage modulus (G'), loss modulus (G'') and angular frequency ($\tan \delta \omega$) In order to describe the rigidity of samples, the complex modulus ($|G^*|$) in Pa has been used for determine this behavior. (Eq. 4.6)

$$G' = (\tau_0/\gamma_0) \cdot \cos \delta \quad \text{in Pa} \quad (\text{Eq. 4.3})$$

$$G'' = (\tau_0/\gamma_0) \cdot \sin \delta \quad \text{in Pa} \quad (\text{Eq. 4.4})$$

$$|G^*| = \sqrt{(G')^2 + (G'')^2} \quad \text{in Pa} \quad (\text{Eq. 4.5})$$

$$\tan \delta = G''/G' = \eta'/\eta'' \quad \text{in Pa} \quad (\text{Eq. 4.6})$$

4.3.1.4 The effect of temperature on viscosity and flow activation energy

Activation energy was calculated using Arrhenius-type equation (eq.4.3)

$$\eta = \eta_{\infty} \exp(Ea / RT) \quad (\text{Eq. 4.7})$$

Where η is the viscosity, η_{∞} is a constant, Ea is the activate energy of flow (J/mol) R is the gas constant, and T is the absolute temperature is K.

4.3.2 Texture measurement for ripening examination

Texture analyzer was carried out by a Texture analyzer model zwick-line type (Zwick GmbH & Co. KG, Germany) (Figure 4.5). It can measure a sample until 5 kg of forces. It equipped with the Kramer shear cell (Figure 4.6), which contain five to ten blade. This cell simulated the single bite on the food stuff in human mouth. The Kramer shear cell method is used mostly for fruit and vegetables, because it can provide the data of fruits characteristic such as bite characteristic, crispiness and firmness. All of them were importance characteristic, which described the texture properties of fruit or fruit product.

Pineapple sample was prepared by slicing at 1 cm thick and using a small tube (radius of 1 cm) to crop the small price of pineapple (Figure 4.7). Fifty grams of pineapple pieces were laid in the Kramer cell. A force was applied at a crosshead speed of 50 mm/min and chart speed of 100 mm/min. The results were reported as chart between resistance force (N) and distance and the mean of maximum force have been calculated. (Figure 4.8) (Bartolomk, 1994) The firmness characteristic can determine by maximum force value. The crispness can determine by the slope for diagram, which claim up. (Shape slope is high crispness)



Figure 4.5 Texture analyzer model Zwick-line

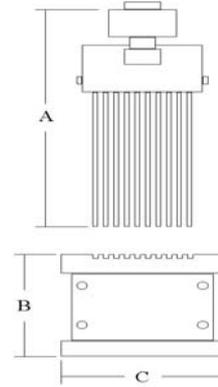


Figure 4.6 Kramer shear set

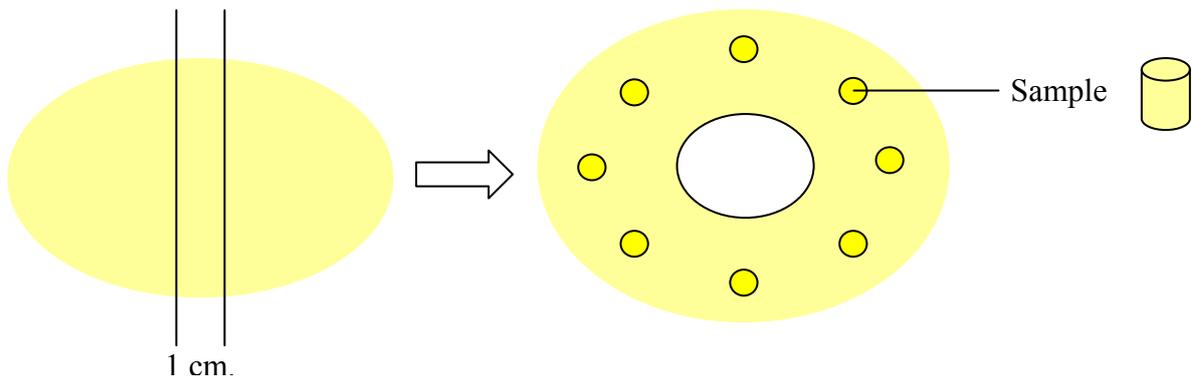


Figure 4.7 Method of sample preparation for texture measurement

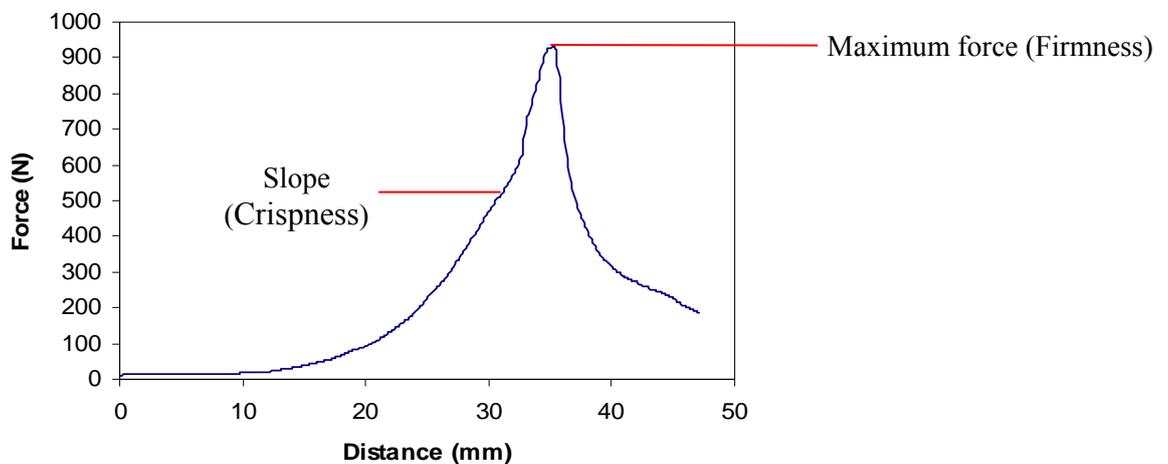


Figure 4.8 Diagram of texture analyze using Kramer shear cell

4.3.3 Method of Color measurement

To study the color changing during fresh pineapple storage, the color measurement was measured by Konica Minolta CR-300 Chroma meter with DP-301 Data processor. (Figure 4.9) The measuring head of CR-300 uses diffuse illumination/ 0° viewing geometry to provide measurements of wide variety of surface with correlate well with color as seen under diffuse lighting condition. This model equipped with a pulsed xenon arc lamp inside a mixing chamber provides diffuse, uniform lighting over the 8 mm-diameter specimen area. The condition of illuminant is CIE illuminant C or D65. In this experiment, illuminant D65 was used to measure the samples. The data was base on three color co-ordinates, namely L a b system. (Figure 4.10) L refer black-white

color. (+ value is white, - is Black). a parameter refer to red-green color (+ is more red, - is more green). b parameter refer to yellow-blue color. (+ is more yellow, - is more blue) The color changed of pineapple can also be expressed as a single numerical value ΔE . This value defines the magnitude of the total color difference. The ΔE value is expressed by the following equation: (Eq 4.8) (Chutintrasri, 2007)

$$\Delta E = \sqrt{(L_0 - L)^2 + (a_0 - a)^2 + (b_0 - b)^2} \quad (\text{Eq 4.8})$$

Where L_0 , a_0 and b_0 represented the reading on target sample color and L , a and b represented the instantaneous individual reading from the sample. For the maturity of pineapple examination, the sample was the pineapple in different phase and target sample was the sample in time zero or phase 1.

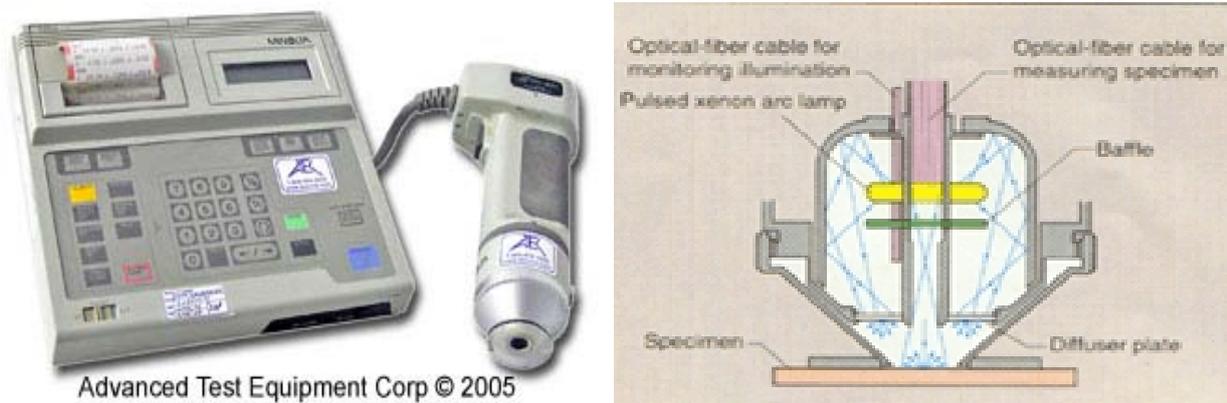
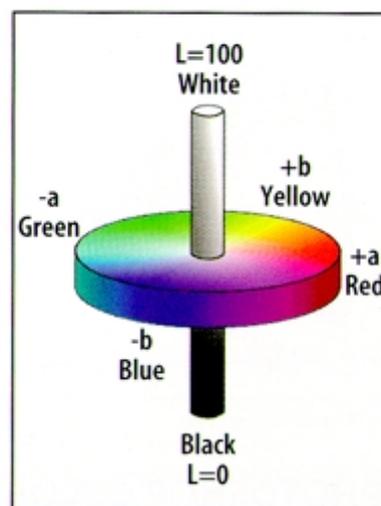


Figure 4.9 Konica Minolta CR-300 Chroma meter with DP-301 Data processor



Lab model

Figure 4.10 Parameter chart of $L^*a^*b^*$ system

Pineapple skin and meat were measured the color method for indicate the ripening level of pineapple. The skin of pineapple was changed from green to yellow, which start from the opposite of crown. The method of color measurement for pineapple skin was used the three points around the biggest circular of pineapple and calculated to mean value. The color of pineapple meat was measured by blending meat with water (4:1, w/v).

4.3.4 pH values

The pH values were measured by using a pH-meter Model CG 840 (Schott Instruments GmbH, Frankfurt, Germany). The fresh pineapple sample was prepared by cut the meat pineapple (without pineapple core) and blending with blender for two minutes. The pH value result was able to determine the changing of acidity of pineapple.

4.3.5 Total solid content (°Brix)

The solid content is able to measurement by using the Reflectometer Jena model II. Fresh pineapple was cut in the middle of fruit (biggest diameter of pineapple fruit). After that, core and skin was removed by ring. 10 g of pineapple was blend for 10 minutes.

4.3.6 Particle size examination for pineapple puree

To investigate the particle size in pineapple puree after and before added gums, the examination was done by using Paticca LA-950 laser scattering particle size distribution analyzer (Retsch Technology GmbH, Haan, Germany) (Figure 4.11a) The reflective index of water and puree was used as 0.1460 the same as using in emulsion. The particle size was report as the specific volume mean diameter ($d_{4,3}$) mode and median size diameter and also the specific surface area (SSA) were calculated by the Horiba software for window version 4.11 (Horiba Ltd., Japan)

The Paricle sizer model Partica LA-950 uses the solid state two light source that was able to be ensured the sufficient scattering over the full angular range (0.01 to 3000 μm) (Figure 4.11b) There are a shape-focus ling wave length red laser source ($\lambda = 650 \text{ nm}$) to measure the large particles up to 3000 μm and a short wave length blue LED laser source ($\lambda = 405 \text{ nm}$) to measure the ultra-microscopic particles up to 0.01 μm . To measure particle size with the laser scattering method, the instrument detects the correlation between the intensity and the angle of light scattered from a particle, then calculates the particle size base on the Mie-scattering theory. The scattering pattern, therefore, is determined by the diameter of the particle relative to the wavelength, not by the absolute diameter of particles. This method provides a high accuracy of ± 0.06 or less compared to standard particle.

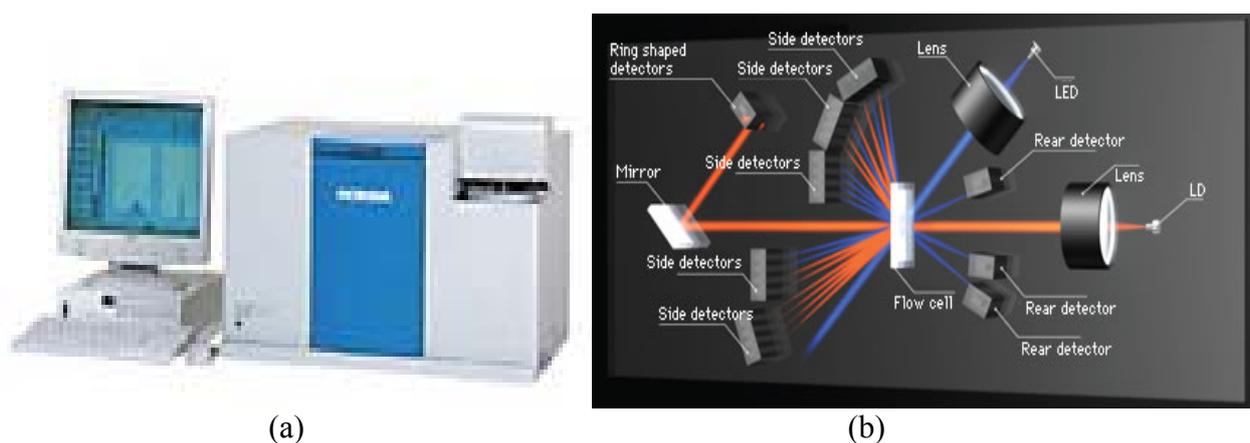


Figure 4.11 (a) Paticca LA-950 laser scattering particle size distribution analyzer, (b) Laser scattering system

4.4 Flow chart of overall experiment

4.4.1. Flow chat of pineapple puree process

Figure 4.12 showed the pineapple puree preparation before added the stabilizers. Before blending, fresh pineapple was prepared by slicing to ring, removing the core and skin. After that, the pineapple was cut into small piece. (size 1 cm^2) In the blending step, the time and speed of blending were major factor controlling rheological properties of puree. Puree after blending removed the fiber, due to fiber interfere the rheological properties of puree. Pineapple puree preserved by freezing at temperature of $-17\text{ }^\circ\text{C}$ in order to stop the enzyme mechanism.

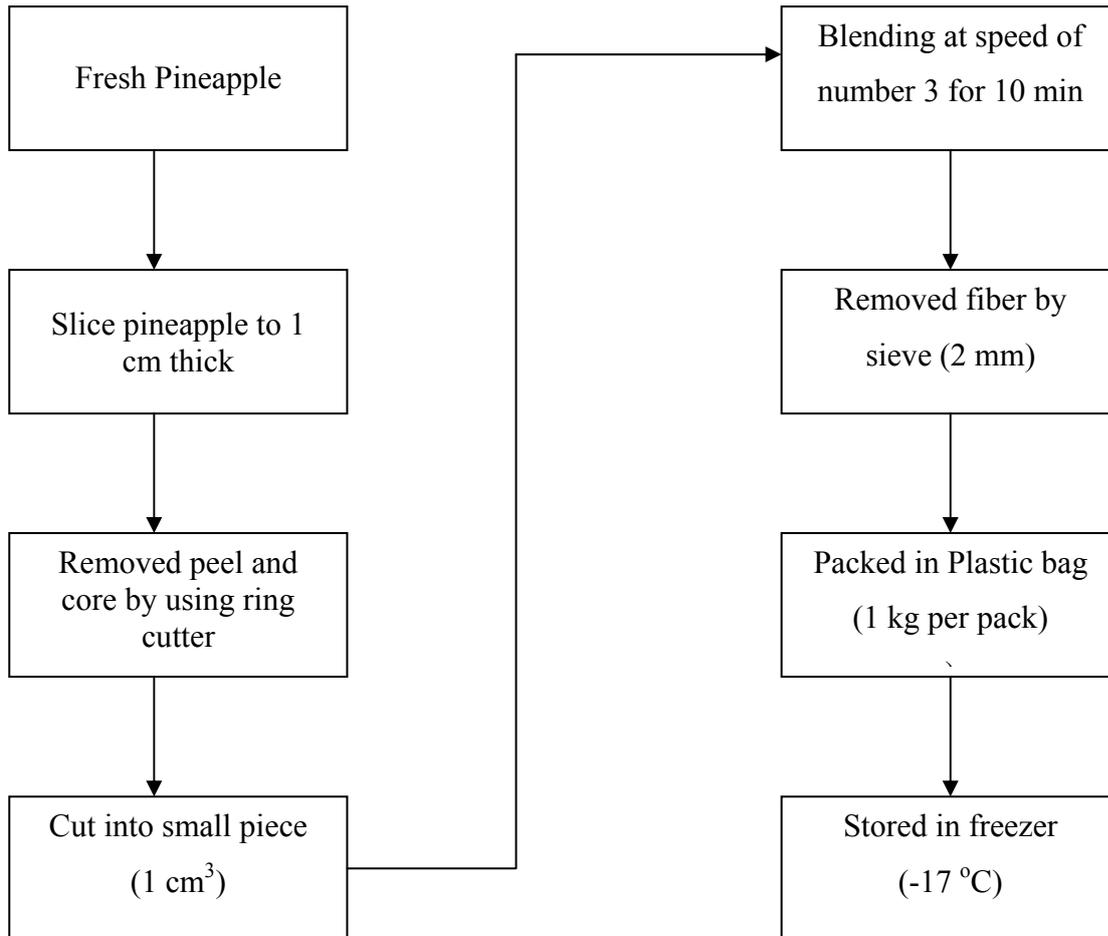


Figure 4.12 Flow chart for preparation of pineapple puree

4.4.2 Flow chart of material science examination of gum solutions

Figure 4.13 showed the overall material science examination of gum solutions, such as pectin, guar gum, xanthan gum and locust bean gum. This figure can be divided into two parts: the part of gum solution preparation. The method of preparation was depend on requirement of each type of gum. For example, locust bean gum required the high temperature in order to completely dissolving. The second part showed type of rheological examination on gum solution: CSR-examination and Oscillation tests.

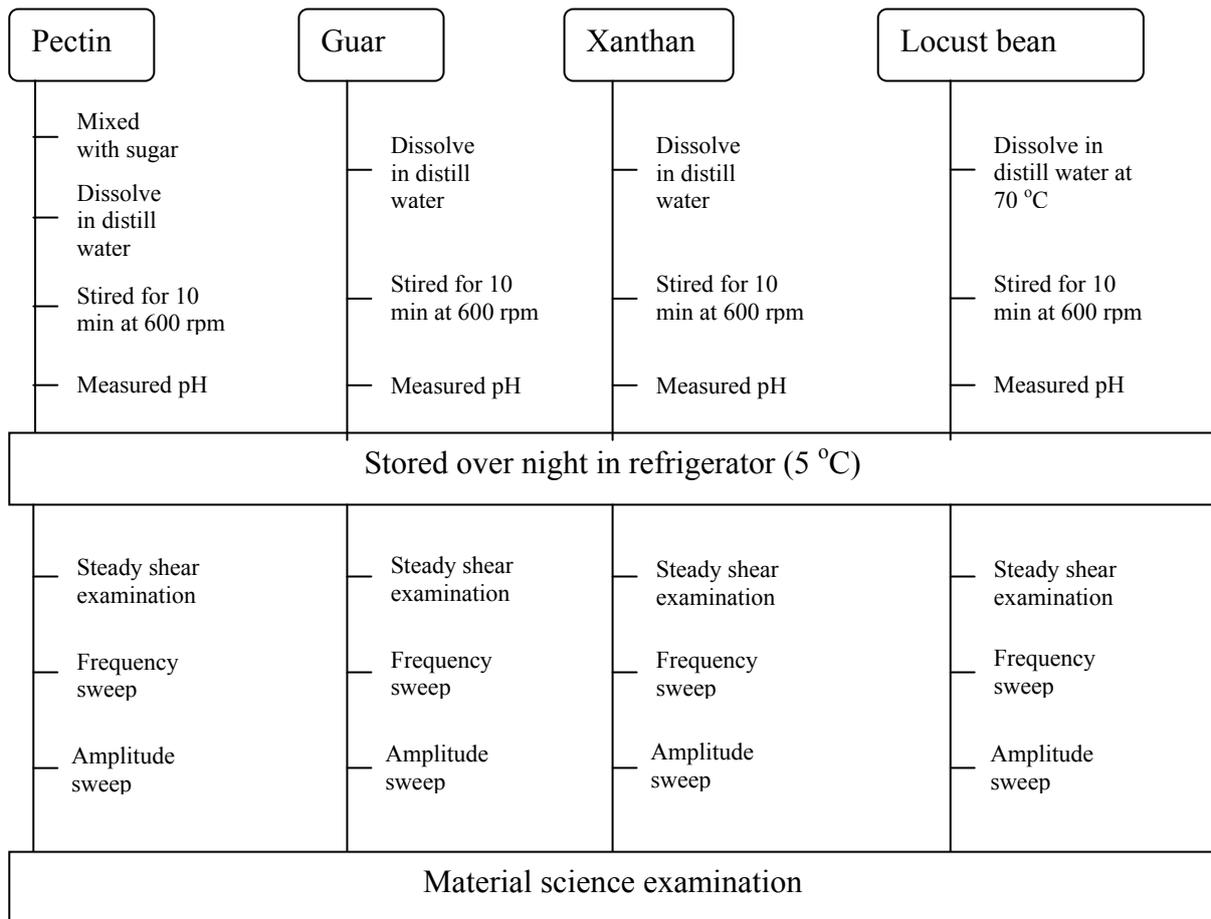


Figure 4.13 Flow chart of gum solution experiment

4.4.3 Flow chart of material science examination on mixed gum solution

Figure 4.14 showed the overall examination of mixed gum solution between galactomannan gums (LBG and guar gum) and xanthan gum. In the preparation part, the xanthan powder and galactomannan gum powder was mixed together at 1 min before dissolve in distiller water. The condition of preparation was depended on type of gums. The mixed gum contains the LBG required high temperature to dissolve in solution. The measurement used the CSR-examination and Oscillation tests.

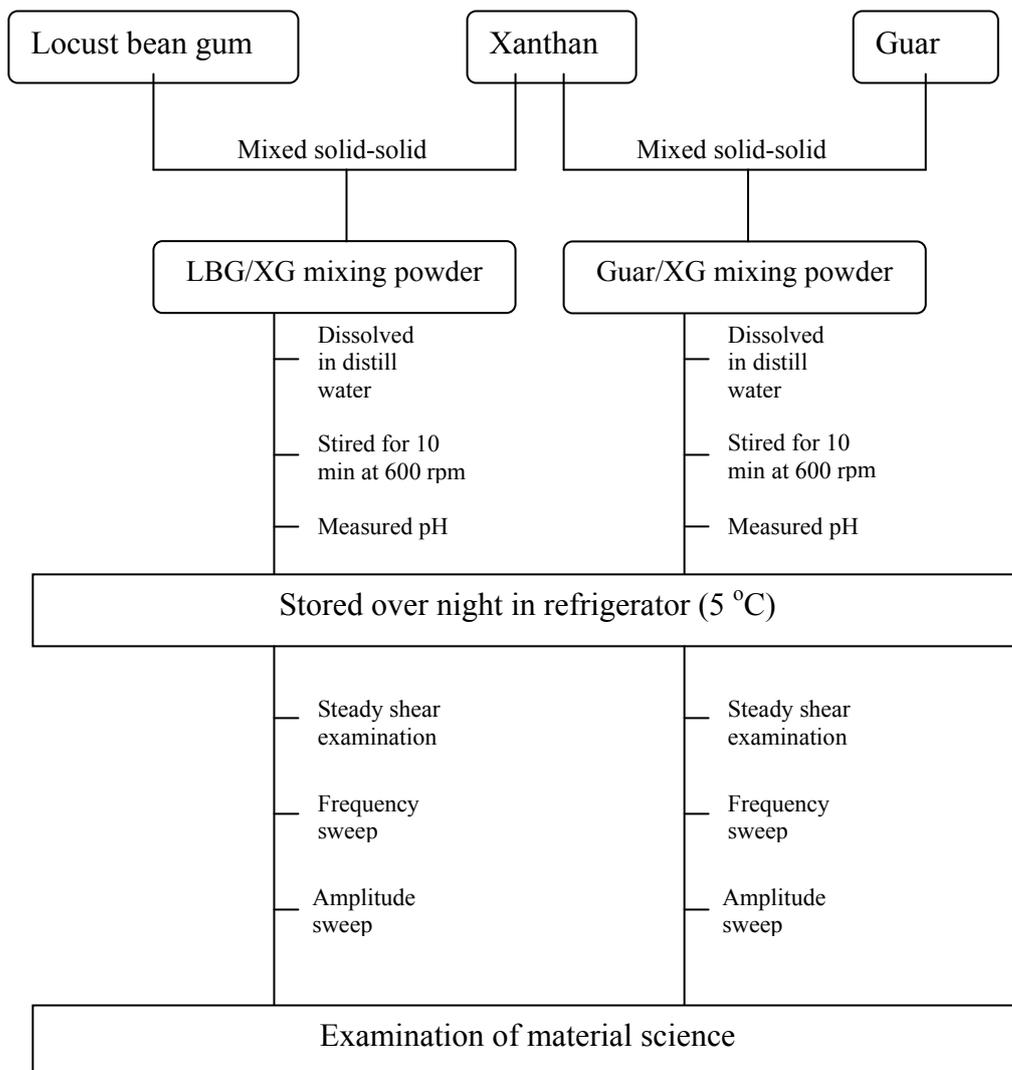


Figure 4.14 Flow chart of mixed gum examination

4.4.4 Flow chart of material science examination on pineapple puree with added gums

Figure 4.15 showed the overall method of examination on pineapple puree added gums, such as pectin, guar, xanthan and LBG. In the preparation part, the requirement of condition was depended on type of gums. Pectin need to mix with sugar before added to pineapple puree in order to increasing dispersion ability. LBG was dissolve completely at high temperature. The rheological measurement used the CSR-examination and Oscillation tests.

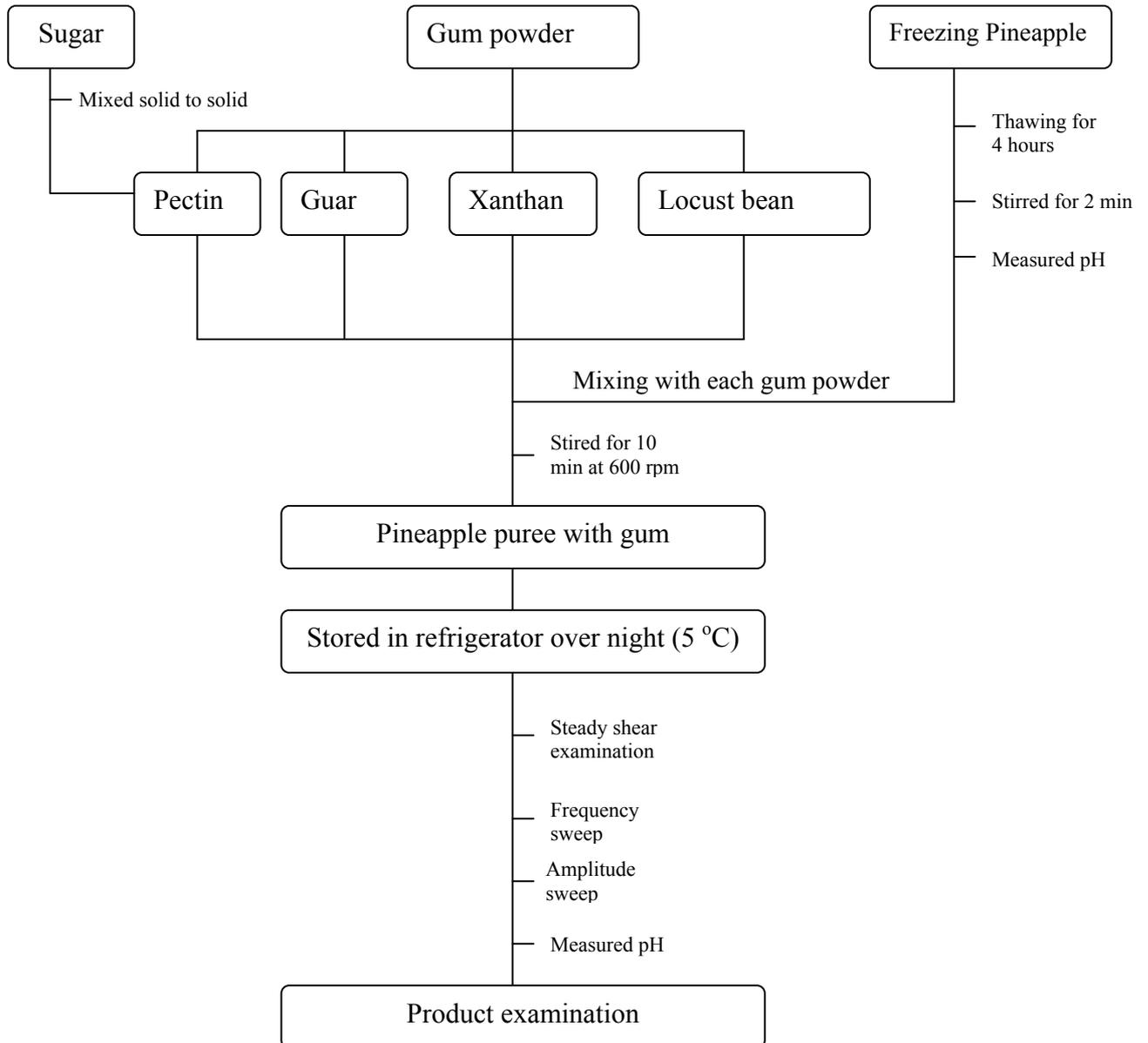


Figure 4.15 Flow chart of pineapple puree with gum experiment

4.4.5 Flow chart of material science examination on pineapple puree with mixing gums

Figure 4.16 showed the overall examination of pineapple puree with mixed gum between galactomannan (LBG and guar gum) and xanthan gum. The two gum powder was mixed before added to pineapple puree. Mixed gums, contain LBG required high temperature in order to completely dissolving. The rheological measurement part used the CSR-examination and Oscillation tests.

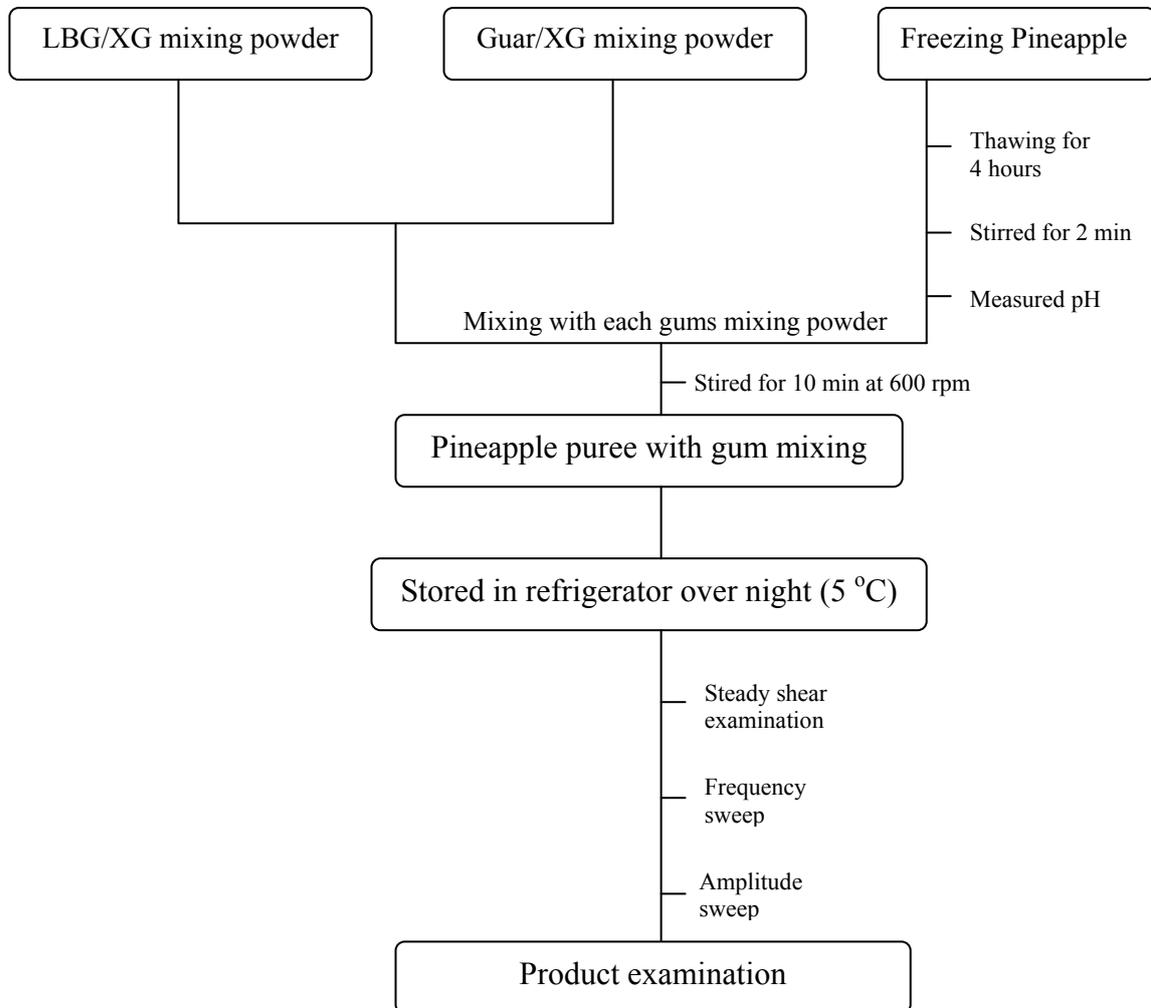


Figure 4.16 Flow chart of pineapple puree added mixed gum experiment

Chapter 5 Material science examination for pineapple fruit

Thailand is one of the world's leading producers and exporters of pineapple. A quality of pineapple for product processing of pineapple depends on mainly the level of maturity mainly. Before use processing it is necessary to check on the pineapple ripening phase, as pineapple at different phase of ripening contain different value of chemicals (sugar content, vitamin content and value of pH) and different physical properties (color properties, texture properties, viscosity). Each product in the process requires a specific quality of material. For example, pineapple puree product needs a very ripening pineapple. In order to classify the characteristics of pineapple into its different level of ripening, the subjective assessment of pineapple by graders necessitates the taking into account of various parameters, for example, color. An objective of this experiment has been the attempt to implement a discriminate analysis on a combination multiple parameters for prediction of pineapple maturity.

5.1. Appearance and color of pineapple fruit

The quality of pineapple changed during storage in refrigerator (5 °C). The first step of pineapple ripening examination was pineapple observation which is a suitable non-destructive method for investigating the ripening of pineapple. The best indicator for non-destructive measurement of ripening was the color of pineapple skin. Normally, skin color of pineapple changed from green to dark yellow. (Smith, 2003) The yellow changing started from the bottom (opposite the crown). (Table 5.1)

Table 5.1 Characteristic of pineapple in five phase of ripening

Phase	pH	TTS (°Brix)	Skin color	Fresh fruit color
1	4.5 a	12.34 a	Dark green (overall)	Light-yellow
2	4.2 b	12.45 b	Yellow beginning (form head)	Light-dark yellow
3	4.0 c	13.53 c	Yellow until head and middle	Yellow
4	3.9 d	13.98 d	Yellow in ¾ of fruit	Dark yellow, some defect
5	3.7 e	14.10 e	Yellow (overall)	Dark yellow and some black spot

*Significant differences were indicated by different letter in same column. (P< 0.05)

According to Table 5.1, it was able to divide the ripening of pineapple into five phases by using the color of skin. The first phase of maturity showed that pineapple skin is dark green. In the second phase of ripening, the skin of pineapple has changed to yellow on the bottom of pineapple. The third phase of maturity showed that half of skin changes to yellow color. In the fourth phase, color of the pineapple skin changed to yellow over 3/4 of skin. Last phase, all of pineapple skin changed to yellow. The Last phase of ripening occurred black spot, was caused by "chilling injury". (Smith, 2003) This is because the sample of this experiment kept in low temperature condition.

Another indicator could determine the ripening phase was pH value. The pH showed the significant value in the different phase. It showed the slightly decreased by started from 4.5 of pH in first phase. In the last phase, the pH value was down to 3.5. One more parameter is the total soluble solid content (TTS) of pineapple which was increased along

with the phase of maturity starting at 12.34 °Brix and increased dramatically at phase 3 of maturity. The cause of this was the increasing of sugar content. Bartolome' (1995) investigated sugar changing during storage on pineapple by freezing at temperature of -18 °C. The result was found that the soluble solid was not changed significantly during storage. The sugar content was also increased with time dependent. (see Fig 5.1 and 5.2)



Figure 5.1 Development of color pineapple skin

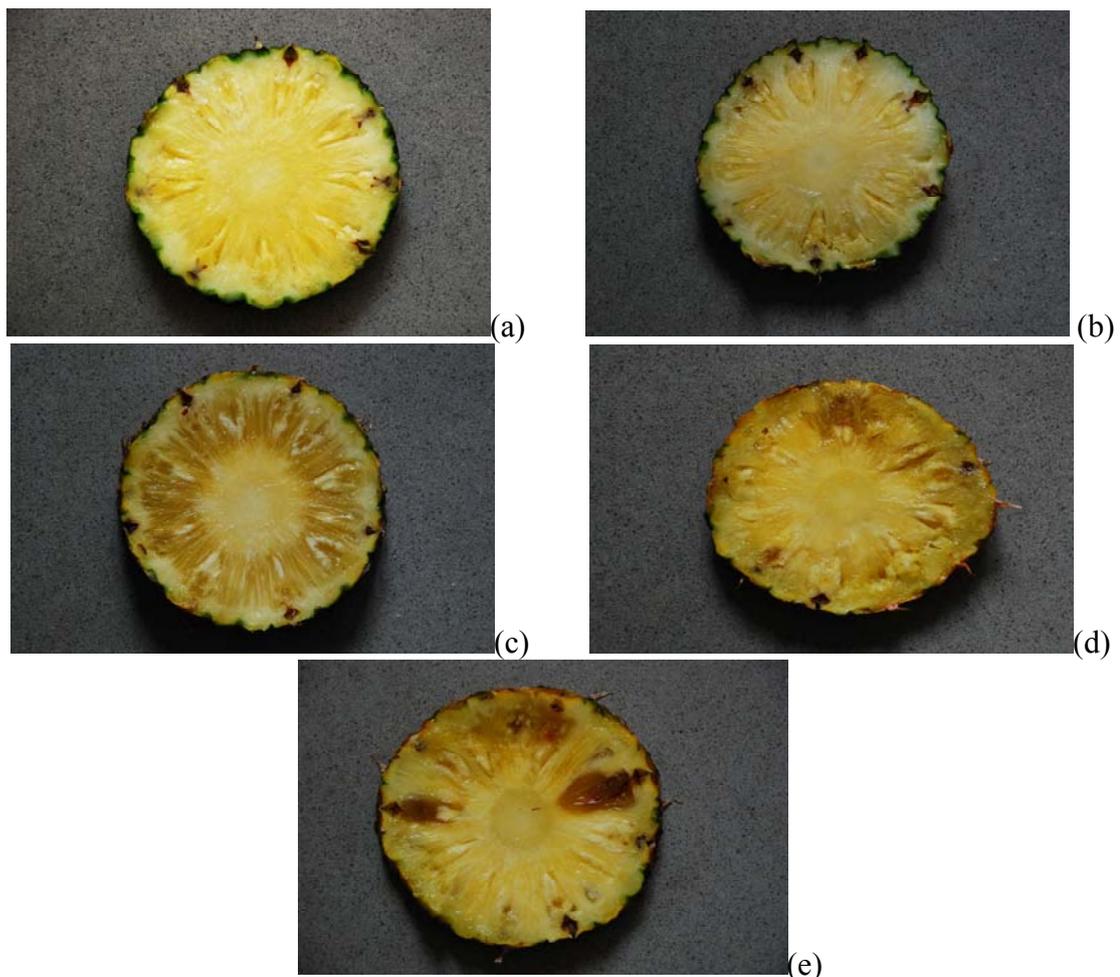


Figure 5.2 Color of pineapple slice in different phases of ripening; Phase 1 (a), Phase 2 (b), Phase 3 (c), Phase 4 (d) and Phase 5 (e)

5.2 Color examination of pineapple pulp

A color of pineapple slice changed in different phase. (Table 5.1; Figure 5.1) The pineapple pulp in the beginning phase was light yellow and particularly the core of pineapple which the light yellow. In second phase, the pineapple pulp was darker yellow than first phase, but the texture and juiciness were not changed a lot. In the third phase, the color of pulp became dark yellow and more juiciness. The texture was softer than previous phase. The fourth phase, pineapple pulp became the dark yellow. The core was softer and a darker yellow color. In the last phase, pineapple pulp became the dark yellow. However, after third phase the pineapple began to have some defects, such as black spot or so called “Black heart”, because of enzyme activity and “chilling injury”. (Smith, 2003; Pathveerat, 2008; Avallone, 2003) There were more and large dark spot in part of pineapple pulp in the high level of ripening. The core became dark yellow. The texture of pulp was softer and had more juicy. It can be explain that pineapple pulp became more juicy, due to the cell wall degradation of pineapple, cell wall became weak and the cell content such as water and sugar leak the to out side cell.

Table 5.2 Color parameter for five phase of maturity

Phase	Color parameter		
	L	a	b
1	45.05 a	-3.88 a	9.00 a
2	44.02 b	-3.84 b	9.05 b
3	40.13 c	-3.57 c	9.44 c
4	34.94 d	-3.19 d	9.55 d
5	30.34 e	-2.59 e	9.62 e

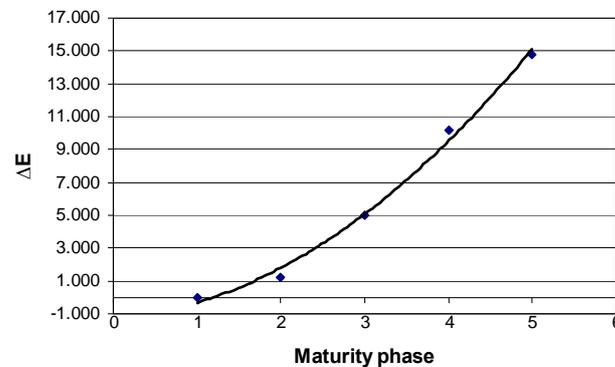


Figure 5.3 Color difference of pineapple with difference phase of maturity

Basically, the color of pineapple pulp was base on yellow color, which is determined by b value. The color of pineapple pulp is mainly able to determine the color changing by Lightness, because the pineapple pulp became darker dependent on time. Therefore, an importance parameter to mainly use for determining the color changing is L value. In the result, the L parameter was decreased with the time or phase of maturity. This experiment, however, was measured only pulp. (Not include the dark spot) The, yellow color parameter, parameter b, was decrease significantly, only slightly decreased. The a parameter, red color parameter, was increased slightly when maturity increased. Therefore, the color of pineapple pulp was changed to become more red color.

The dark color of pineapple was also called “The internal browning reaction, because of enzymatic reaction of polyphenoloxidase, laccase and peroxidase. (Soares, 2005; Avallone, 2002) The enzyme activity changed the reducing sugar to the browning pigment. The most polysaccharides, such as pectin, hemicellulose and cellulose located in cell wall of pineapple. (Smith, 1995; Manganris, 2005) When pineapple is ripened, the cell wall of pineapple loss the strong structure and the cell contents such as sugar leak to out side the cell. After that, the enzymes, those locate outside the cell, activated with sugar and turn to browning pigment. These can explain the occurrence of black spot in pineapple slice.

The total color different (ΔE) (Figure 5.3) was used for investigating the changing of over all color on pineapple pulp. The trend of overall color was increased significantly from 0 to 15 with level of ripening. In this case, the equation matched the trend line of ΔE closely was the polynomial equation (Eq 5.1)

$$\Delta E = 0.5845 \cdot (\text{MP})^2 + 0.3554 \cdot (\text{MP}) - 1.2507 \quad r = 0.996 \quad (\text{Eq 5.1})$$

5.3 Texture examination for pineapple ripening

The shear force for chewing pineapple slice was measured using the Kramer shear cell. In order to investigate the structure of pineapple in different phase of ripening, texture of pineapple in five phase of ripening was measured. The texture data described the two main characteristic of the firmness and crispness of the pineapple slice in different level of maturity. The firmness determines by the maximum force or the top of the peak in the diagram between forces and distance. The crispness was described by slope of diagram between start of diagram to reach the peak. The measurement parameters on texture are shown in Table 5.3.

Table 5.3 Texture parameters of pineapple fruits in different phase

Phase	F_{max} N	$s (0.1 \text{ to } F_{max})$ mm	Slope N/mm	A_T N·mm
1	993.7	35.2	53.34	5992
2	866.0	35.0	46.34	5227
3	828.1	35.3	46.08	5161
4	808.0	35.3	43.06	4803
5	656.9	34.4	36.46	3698

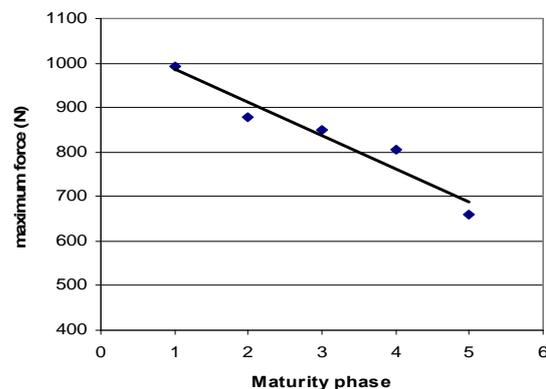


Figure 5.4 Trend line of maximum force on pineapple in different phase

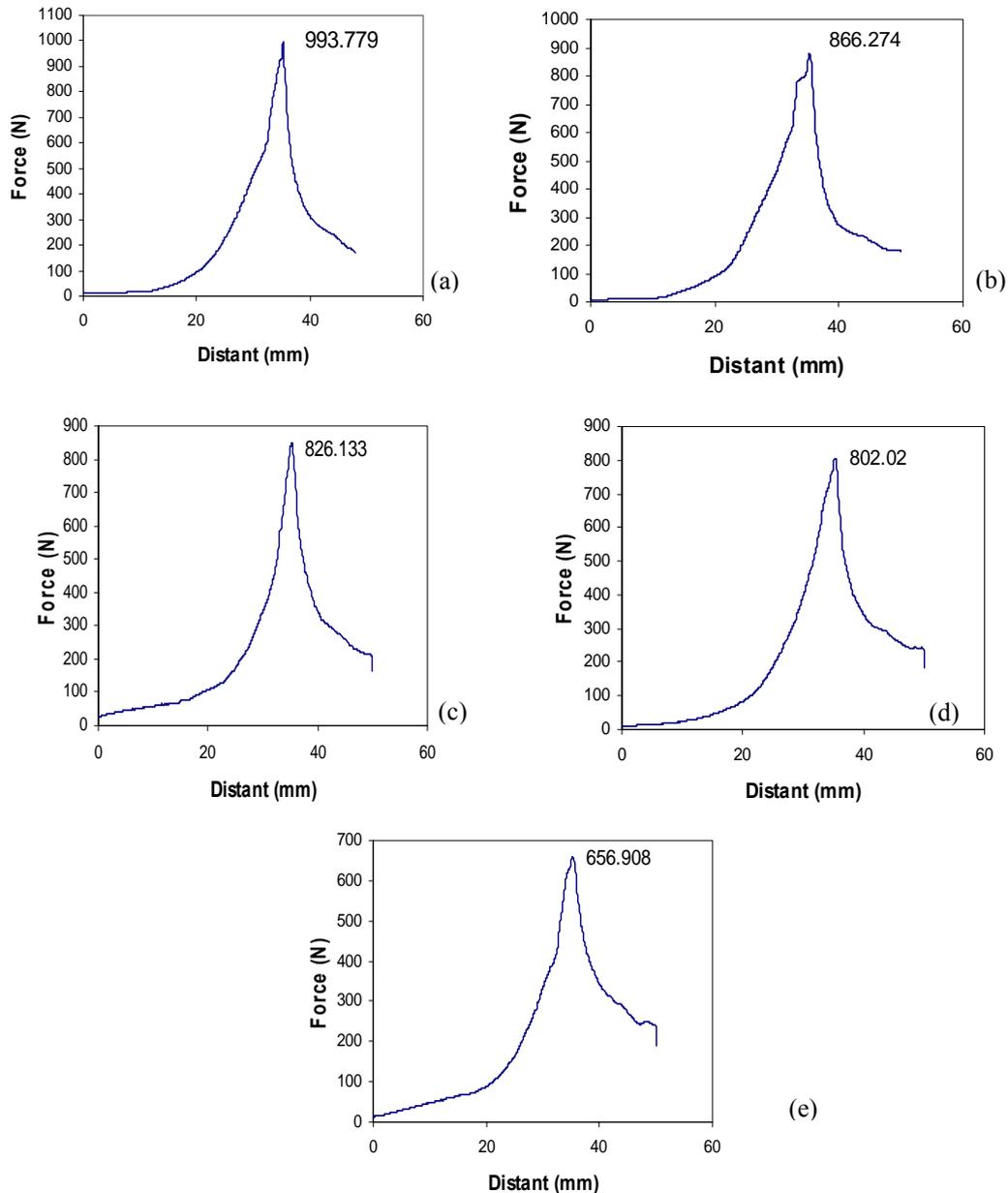


Figure 5.5 Diagram of texture analyze of five phase of ripening; phase 1(a), phase 2 (b), phase 3 (c), phase 4 (d) and phase 5 (e)

The result showed that the maximum force decreased when ripening of pineapple was increased (Fig. 5.5) Therefore, the firmness of pineapple was decreased when the level of maturity was developed. That can be explained by the structure of pineapple being destroyed during storage or during the change in the ripening phase. According to table 5.3, the slopes decreased with the increasing phase of maturity, but it did not change significantly. Thus, the crispness of pineapple fruit does not depending on the phase of maturity. Area of diagram showed a decreasing value with increasing phase of maturity. The area under diagram can describe to toughness (Bourne, 2002), so the toughness of pineapple fruit decreased with each phase of maturity. In conclusion, the ripening of pineapple fruit mainly determines using the maximum force or firmness. According to

Gonzalez-Aguilar (2004), the quality of pineapple has been measured firmness by maximum rupture force of texture analysis.

The maximum force that changed with time or phase of ripening showed a decreased trend line and range from 993.77 to 659.16 N. (Fig. 5.4) The firmness of pineapple fruit in different phase of maturity could predicted by the linear equation (Eq. 5.2)

$$F_{\max} = -74.171 \cdot (\text{MP}) + 1059.6 \quad \text{in N} \quad r = 0.965 \quad (\text{Eq 5.2})$$

Whereas, MP is maturity phase

Pathaveerat, Terdwongworakul and Phaungsombut (2008) also classified the maturity of pineapple by using the multivariate data analysis. Pineapple was classified by using various methods. The pineapple was divided into three groups by the level of translucent yellow: low, medium and high value of translucent yellow. The texture analyze was one method used for analyzing pineapple properties of each group. The firmness was determined by compression test method. Their results showed that the firmness of pineapple decreased when pineapple matured to the next phase. Non-maturity showed the high firmness. The next phase of maturity showed a lower force value than for the first phase. The third phase performed that the force of compression showed the lowest value. In the Comparison with our result, both results were similar, as the firmness decreased with time or phase of maturity.

Chapter 6

Material science examination of selected gums

The aim of this study was to determine the rheological properties of selected gums before application of the gum into pineapple puree. This study investigated the rheological properties of pectin, locust bean gum, guar gum and xanthan gum. In addition the effects of factors such as concentration and temperature on rheology of gums were observed. Furthermore, the interaction between galactomannan and xanthan gum was carried out to investigate the synergistic effect of gum mixing. The rheological properties were carried out by using the control shear rate examination and the oscillation test.

6.1 Examination of pectin solution

Pectin was the one of thickening agent. Pectin has specific factor on rheological properties, such as condition factor or characteristic of pectin factor. The effect of different factors, such as type of pectin, level of DE, temperature, concentration of pectin and concentration of Ca-ion was investigated. To study the structure of pectin on those influences, rheological methods were applied in order to analyze the stability properties, viscosity properties and gelling properties.

6.1.1 Effect of type of pectin solution on rheological properties

Pectin is divided into two groups by its sources of production. The main source for pectin uses the apple puree and citrus peel to extract the pectin powder. The apple pectin in this study was represented by apple pectin, coded "AU202", DE level was 70.5. The citrus pectin was represented by citrus pectin, "coded "CU201", DE level was 70.5. The comparison made using the concentration of pectin, which 1 % and added 10% of sugar.

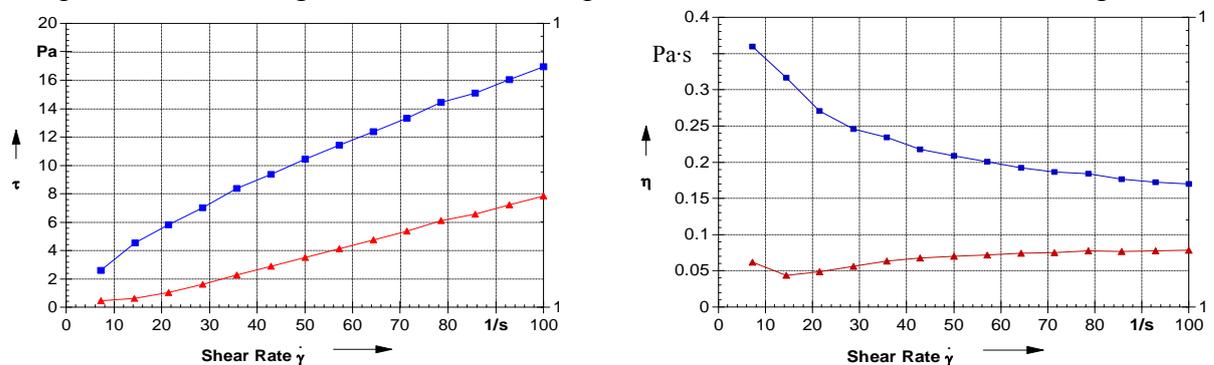


Figure 6.1 CSR-Examinations of shear rate examination for apple (▲) and citrus (■) pectin solution at 20 °C

Table 6.1 Rheological parameter for citrus pectin with different level of DE at 20 °C

Type of Pectin	DE	OW						HB				
		K $Pa \cdot s^n$	n -	r -	A_{TH} Pa/s	η_{eff} (50/s) $Pa \cdot s$	τ_0 Pa	K $Pa \cdot s^n$	n -	r -	η_{eff} (50/s) $Pa \cdot s$	-
Apple	70.5	0.28	0.752	0.988	28	0.091	√ -1.16	0.11	0.972	0.999	0.091	-
Citrus	70.5	1.57	0.508	0.978	148	0.163	√ 0.61	0.53	0.751	0.949	0.174	-

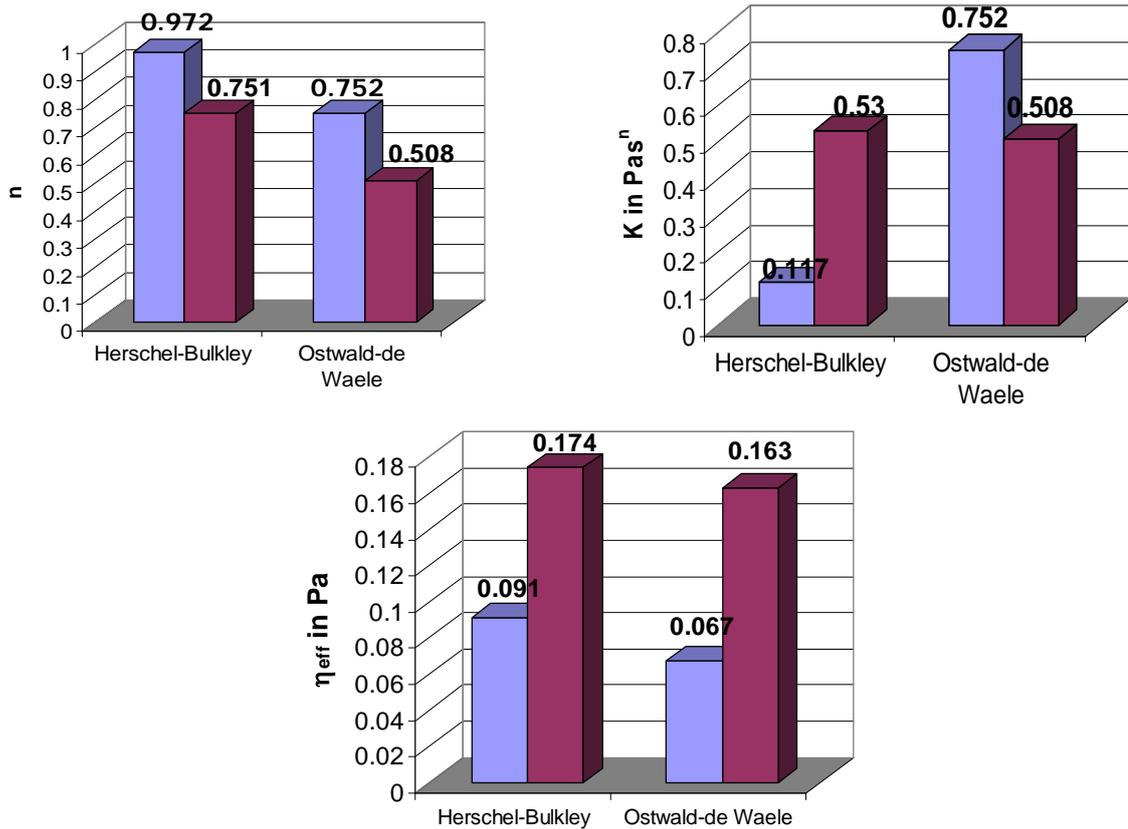


Figure 6.2 Comparison of rheological parameter for apple pectin (■), citrus pectin (■)

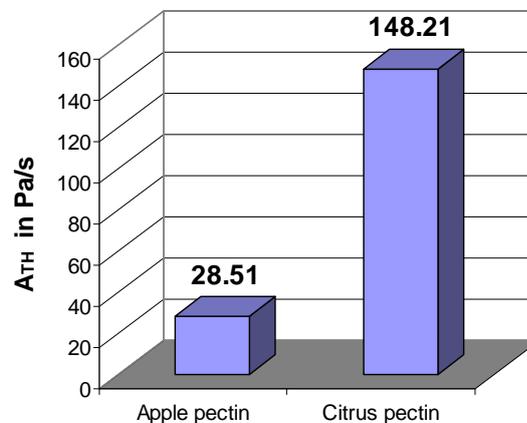


Figure 6.3 Comparisons the thixotropic area between apple and citrus pectin

The rheological properties were used for analyzing the structure of pectin. The studies emphasized stability and viscosity. The Herschel-Bulkley and Ostwald-de Waele models were used for matching the rheological parameters. Results showed that both model exhibited high r value on apple and citrus pectin. ($r > 0.950$) The yield point of apple pectin exhibited a negative value. In contrast, citrus pectin showed a positive value of yield point. Thus, the Ostwald-de Waele model was used for matching the rheological parameters of pectin. The yield point is related to the existence of a reticulated structure, which is generally due to the interaction between colloid particles or the formation of link between the long chain molecules. (Alonso et al., 1995) In this study, the yield point of citrus pectin show the positive. It may be that citrus pectin was able to make the stronger structure than

apple pectin. This theory was supported by the data of citrus pectin flow index which was lower than that of apple pectin. Therefore, citrus pectin was stronger and more stable than apple pectin. For consistency factor (K), there is no trend of K value, however, the range was between 0.18 to 0.752. In a comparison between two types of pectin, viscosity of citrus pectin was higher than that of apple pectin base on Herschel-Bulkley model. From figure 5.2 showed thixotropic area: the citrus pectin exhibited the higher than apple pectin. This is because the citrus pectin used the higher energy for rupture the structure.

6.1.2 Effect of level of DE in different types of pectin

The pectin was also classified by using the level of DE (Degree of esterification), such as high (More than 70), medium (around 50) and low (lower than 10) level of DE. Basically, rheological properties of pectin changed along with the level of DE. From previous experiments (Type of pectin experiment), the citrus pectin was chosen to represented the samples for the effect of DE, because the DE of citrus pectin was lower than that of apple pectin. The level of DE content was divided into three levels. The high level of DE group represented by citrus pectin, DE of 70.1 (coded "CU201). The medium level of DE represented by citrus pectin, 35.1 of DE (Coded "CU701") The low level of DE group represented by citrus pectin, 9.6 of DE (coded "CU902). In addition, the amide pectin was also compared with other types of pectin, represented by citrus pectin, DE of 49.9 (Coded "CU L063/05)

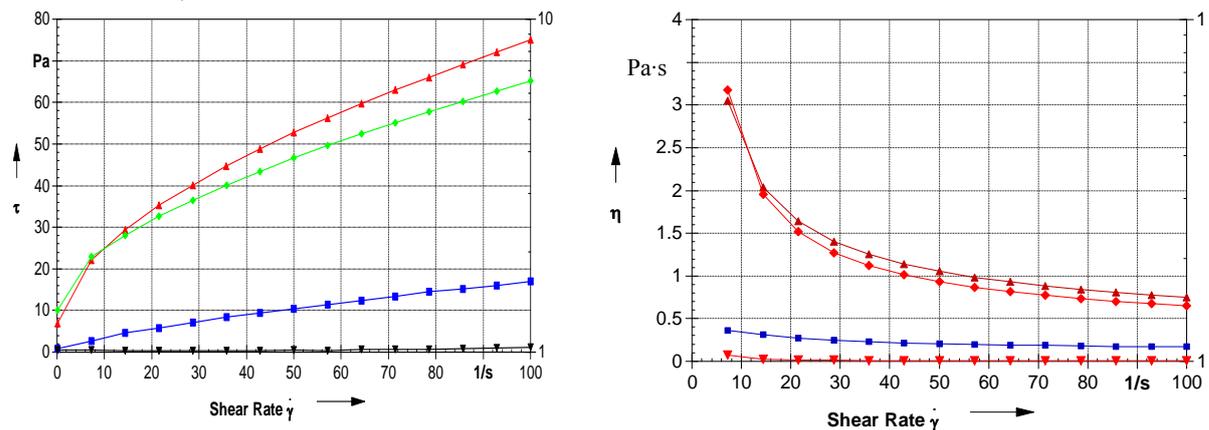


Figure 6.4 CSR-Examination for pectin with different level of DE; CU201 (■), CULO63/05(▲), CU701 (◆) and CU902 (▼)

Table 6.2 Rheological parameter for citrus pectin with different level of DE at 20°C

Type	DE	OW					HB						
		K $Pa \cdot s^n$	n	r	A_{TH} Pa/s	η_{eff} (50/s) $Pa \cdot s$	τ_0 Pa	K $Pa \cdot s^n$	n	r	η_{eff} (50/s) $Pa \cdot s$		
CU 902	9.3	0.026	0.874	0.534	33.5	0.023	-	0.35	0.001	0.987	0.963	0.009	√
CU701	35.1	2.184	0.713	0.961	745	0.505	-	0.52	0.579	0.968	0.993	0.582	√
CU201	70.1	1.578	0.508	0.978	143	0.174	-	0.61	0.530	0.951	0.994	0.164	√
CU L063/05	49.9	12.691	0.386	0.97	933	0.784	-	5.41	5.166	0.579	0.989	0.751	√

Results showed the influence of DE on rheological properties of pectin. (Table 6.10) The Herschel-Bulkley and Ostwald-de Waele models were used for matching rheological parameters and curves of all samples. (Figures 6.3 and 6.4) Results showed that the curve (Figure 6.3) and rheological parameters were good fit with both models ($r > 0.950$). However, pectin at all level of DE exhibited positive yield point value (τ_0), so yield point

must be considered to calculate the viscosity. Thus, the Herschel-Bulkley model was matching closely. The flow index (n) value depended on the DE value. As can be seen, the flow index of pectin was decreased with an increasing of level of DE. This means that pectin with high level of DE exhibited a strong and stable structure. Moreover, the yield point also increased with level of level of DE. According to Imeson (1994), the high methoxy pectin (also known as high degree of esterification) was the best as the gelling agent. When pectin was modified to reduce the degree of esterification, pectin exhibited the slow set gel. Therefore, this can be described that the pectin with high level of DE is able to set gel with strong structure. The viscosity of pectin does not depend on the level of DE. It can be seen that the highest viscosity was in the pectin with medium range of DE. (35.5) The lowest viscosity was in pectin with low range of DE.

In the case of amide pectin with medium range of DE (49.9), pectin showed low flow index and high yield point compare with other pectin. This can be described that the amide pectin exhibited a strong structure and set gel. Manuel *et al* (2001) studied the rheological behavior of amide pectin. The amide pectin was the one of the gelling agents and set the gel at pH 3.3 to 3.8.

6.1.3 Effect of Ca-ion on pectin properties

To study the effect of Ca-ion on the pectin properties, Calcium lactate has been added to pectin in term of the weight of Ca-ion. (mg/g) The Ca-ion was applied to two level of DE: pectin with low DE and high DE using 40 and 80 mg of Ca-ion. Moreover, the modified type of pectin (amide pectin) was also considered for studying the effect of Ca-ion on rheological properties. The control sample of each type of pectin used pectin solution without Ca-ion added.

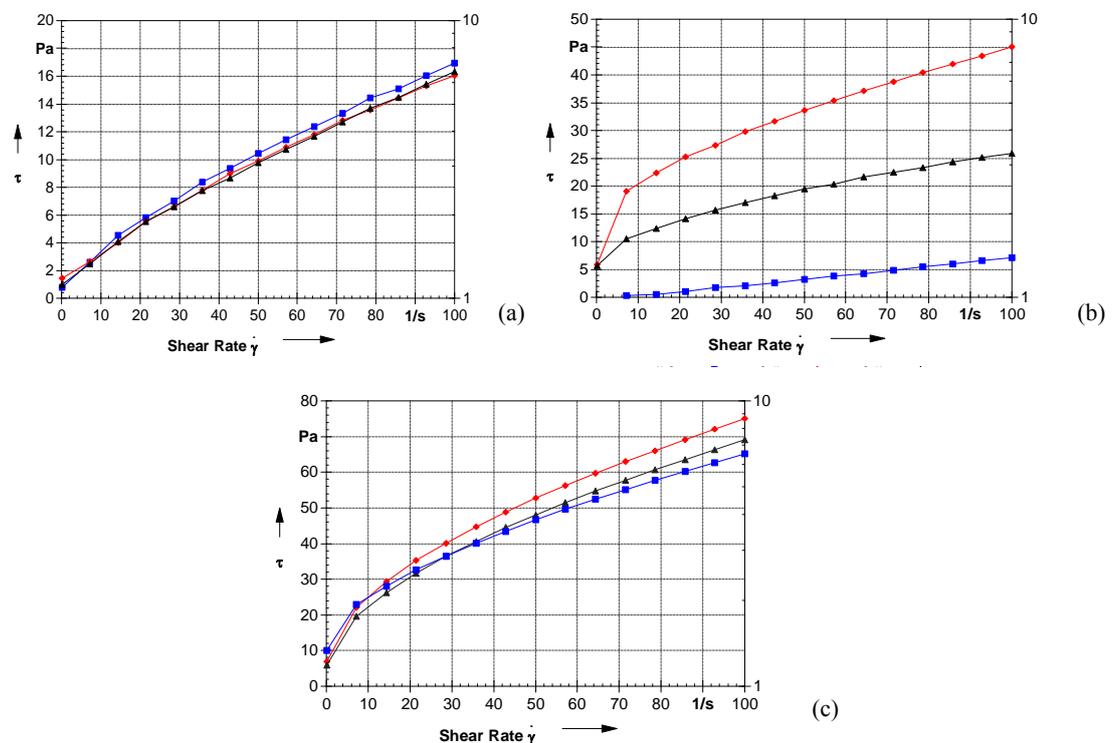


Figure 6.5 CSR-Examination for different types of pectin; High-DE pectin (a), Low-DE pectin (b) and Amidate pectin (c) in different Ca-ion; no Ca-ion (■), Ca-ion 40 mg. (▲) and Ca-ion 80 mg. (◆)

Table 6.3 Rheological parameters of pectin containing different of Ca-ion on pectin

Type	Ca-ion (mg)	OW					HB				
		K Pa·s ⁿ	n	r	η_{eff} (50/s) Pa·s	τ_0 Pa	K Pa·s ⁿ	n	r	A _{TH} Pa/s	η_{eff} (50/s) Pa·s
High-DE	0	1.57	0.508	0.973	0.163	0.60	0.53	0.751	0.994	148	0.174
	40	0.92	0.629	0.992	0.167	0.52	0.71	0.689	0.994	155	0.175
	80	1.76	0.471	0.958	0.154	0.85	0.40	0.798	0.995	116	0.167
Low-DE	0	0.38	0.590	0.885	0.058	0.21	0.07	0.999	0.996	72	0.072
	40	6.43	0.331	0.798	0.296	5.92	1.47	0.593	0.840	207	0.285
	80	18.17	0.258	0.808	0.596	5.03	7.34	0.455	0.811	1,010	0.647
Amidate	0	15.18	0.312	0.961	0.639	8.59	4.27	0.568	0.993	745	0.671
	40	12.76	0.368	0.973	0.695	4.93	4.40	0.590	0.993	827	0.717
	80	12.69	0.386	0.970	0.751	5.41	5.16	0.575	0.989	933	0.784

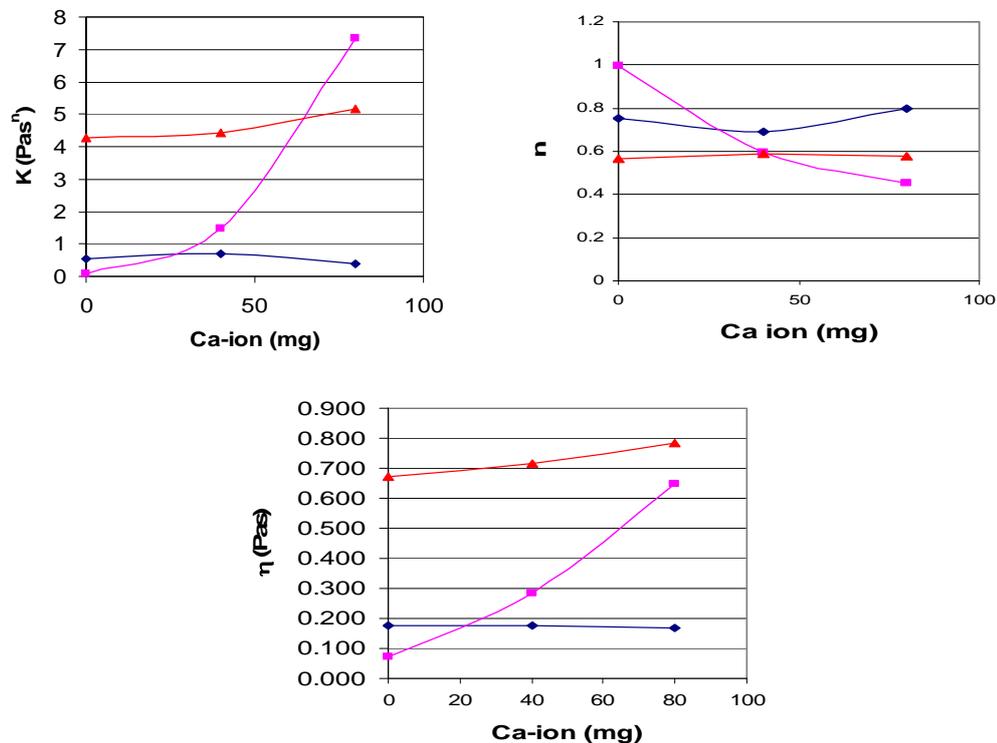


Figure 6.6 Trend of rheological parameters of pectin in different Ca-ion contents; High-DE pectin

(♦), Low-DE pectin (■) and Amidate pectin (▲)

From Table 6.3, the Herschel Bulkley and Ostwald-de Waele models of all samples exhibited high value of r parameter, so both models had the potential to matched parameters. The Herschel-Bulkley model matched pectin with all level different of Ca-ion, because yield point exhibited a positive value. In the table 6.4, the thixotropic area of pectin increased with level of Ca-ion. That means that the pectin solution needed used high energy to break the structure when added high Ca-ion in pectin solution. From data, low-DE pectin with added Ca-ion 80 used significantly high energy and exhibited a strongly gel structure.

Results (Table 6.3, Figure 6.4) showed that high-DE pectin did not exhibit a good reaction with the Ca-ion, because all of the rheological parameters showed no change significantly. It showed an evident that all parameters of high-DE pectin did not change significantly when level of Ca-ion increased. In contrast, the rheological properties of pectin

with low level of DE were changed significantly. As can be seen in figure 6.4, the flow index of low-DE pectin decreased with level of Ca-ion. The consistency factor and viscosity increased with level of Ca-ion. Therefore, low-DE pectin showed strong structure and exhibited the gel system when added high Ca-ion. In case of amide pectin, Ca-ion showed slightly affected on rheological properties of amide pectin. The consistency factor and viscosity slightly increased with level of Ca-ion. The flow index decreased with level of Ca-ion.

The reason for this concerned the binding ability of pectin structure. The high-DE pectin has a “smooth” long linear of homogalacturonan and rhamnogalacturonan. (Slavov *et al.*, 2009) In other word, high-DE pectin has a smaller free carboxyl group for binding with Ca-ion. In contrast, low-DE pectin has a capacity to bind with calcium ions and to be cross-link through these Ca-ions when consecutive free carboxyl groups are present in sufficient number. (Vorgen *et al.*, 1995) The binding between pectin and Ca-ion is called “Egg box” model. There is its galactomannan chain in the 2_1 helical conformations, but in solution, the 3_1 helical forms are also possible. (Rigby *et al.*, 2000) According to Capel *et al.* (2006) studied the Calcium induced gelation of amidated pectin. Their results found that amidated pectin had little influence on the sensitive to Ca-ion the same as our results.

6.1.4 Effect of pre-heat process experiment

The influence of pre-treatment effect of pectin preparation on structure was studied using their rheological properties. The pre-treatment was used in this study which the heating effect. After being dissolved in distilled water, the pectin was heated to 70 °C. In this experiment, samples were divided into two cases: non-heat and heat. Pectin was represented by using a high-DE group and low-De group. The amide pectin group was also included when investigate this effect. All of samples of pectin solution had the 40 mg of Ca-ion added.

Table 6.4 Rheological parameter for effect of heating on pectin preparation

Type	Trt.	OW					HB				
		K Pa·s _n	n	r	η_{eff} (50/s) Pa·s	τ_0 Pa	K Pa·s _n	n	r	A	η_{eff} (50/s) Pa·s
High-DE	N	0.92	0.629	0.992	0.167	0.043	0.71	0.689	0.994	155.36	0.170
	H	1.46	0.515	0.973	0.157	0.204	0.61	0.712	0.993	151.07	0.166
Low-DE	N	14.1	0.331	0.908	0.651	5.031	7.34	0.455	0.911	1010.3	0.647
	H	10.1	0.3541	0.934	0.514	1.437	7.67	0.4	0.929	931.01	0.499
Amidate	N	16.4	0.302	0.947	0.693	9.056	4.93	0.543	0.947	706.52	0.692
	H	10.6	0.398	0.888	0.671	8.589	4.27	0.568	0.954	745.41	0.671

* N = Non-heating, H = Heating

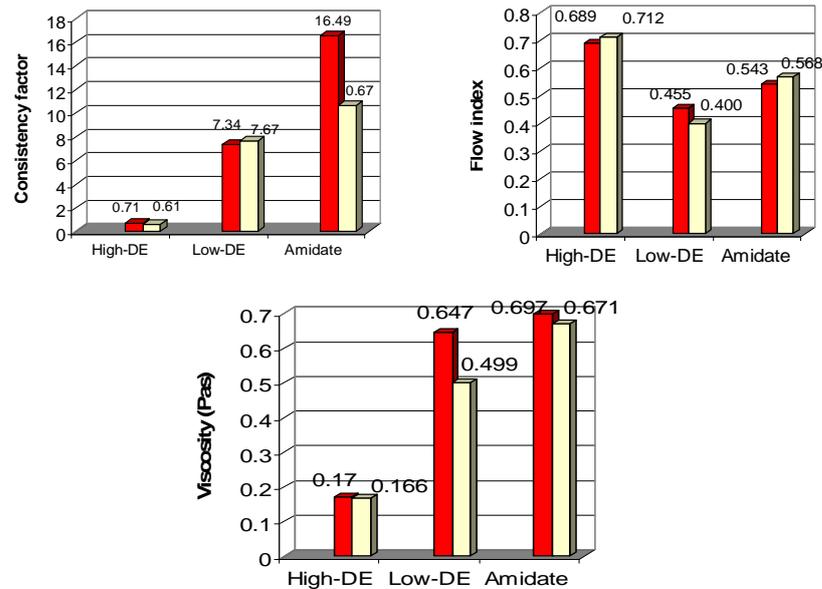


Figure 6.7 Comparison of rheological parameter for pectin with different pre-treatment; Non-heat (■) and Heat (□)

The Herschel-Bulkley and Ostwald-de Waele model models were used for describing the curve and parameters. Both showed high value of r at all samples ($r > 0.900$) However, the samples exhibited a positive value of yield point (τ_0), so the Herschel-Bulkley model was closely matched samples. Results showed that the pre-heating treatment has little influence on normal pectin: both high and low-DE. It can be seen that these were not changed significantly. However, the viscosity of heating sample was slightly decreased. Therefore, the stable of pectin structure was not depended on the pre-heating process.

6.2 Rheological properties of Locust bean gum solution

Locust bean gum (LBG) is one stabilizer of galactomannan groups. It widely used in several industries, such as bakery, confectionary industries. The properties of locust bean gum depended on factors: concentration of locust bean gum and temperature. The Aim of this study was to investigate the rheological properties of locust bean gum. This study was emphasized its stability and viscosity properties.

6.2.1 Effect of concentration on LBG

To study the effect of concentration LBG on rheological properties, the concentration of LBG has been investigated at 0.2, 0.4, 0.6, 0.8 and 1 % using the rheological method of control shear rate examination. The pH of LBG was adjusted to 3.5. In this study, the rheological properties was measured by adapting Double gap set with 1 state method of measurement, with shear rate up to 1000/s, as LBG has a potential to exhibit the property low viscosity.

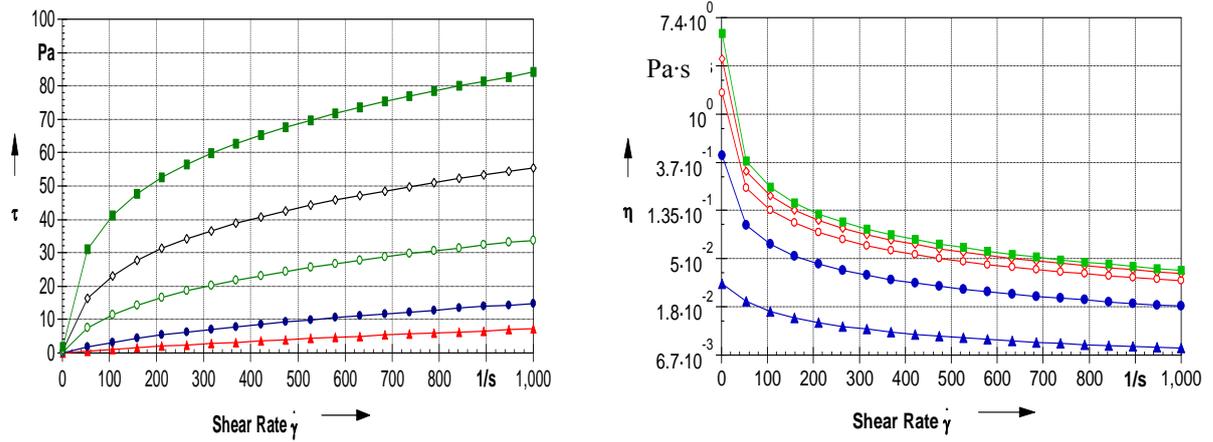


Fig 6.8 CSR-Examiantion (1 phase) of shear rate on LBG in different concentration; 0.2 % (\blacktriangle), 0.4 % (\bullet), 0.6 %(\circ), 0.8 % (\diamond) and 1 % (\blacksquare)

Table 6.5 Rheological parameters of the concentration LBG solution

c %	OW				HB						
	K Pa·s ⁿ	n	r	η_{eff} (1000/s) Pa·s	τ_0 Pa	K Pa·s ⁿ	n	r	η_{eff} (1000/s) Pa·s		
0.2	0.01	0.921	0.986	0.009	√	-0.008	0.02	0.854	0.999	0.010	-
0.4	0.04	0.933	0.993	0.036	√	-0.086	0.124	0.697	0.998	0.030	-
0.6	0.31	0.702	0.928	0.080	√	-1.184	1.401	0.469	0.998	0.110	-
0.8	0.987	0.611	0.911	0.164	√	-4.77	5.420	0.350	0.999	0.224	-
1	2.5113	0.534	0.899	0.293	√	-15.40	17.401	0.255	0.999	0.409	-

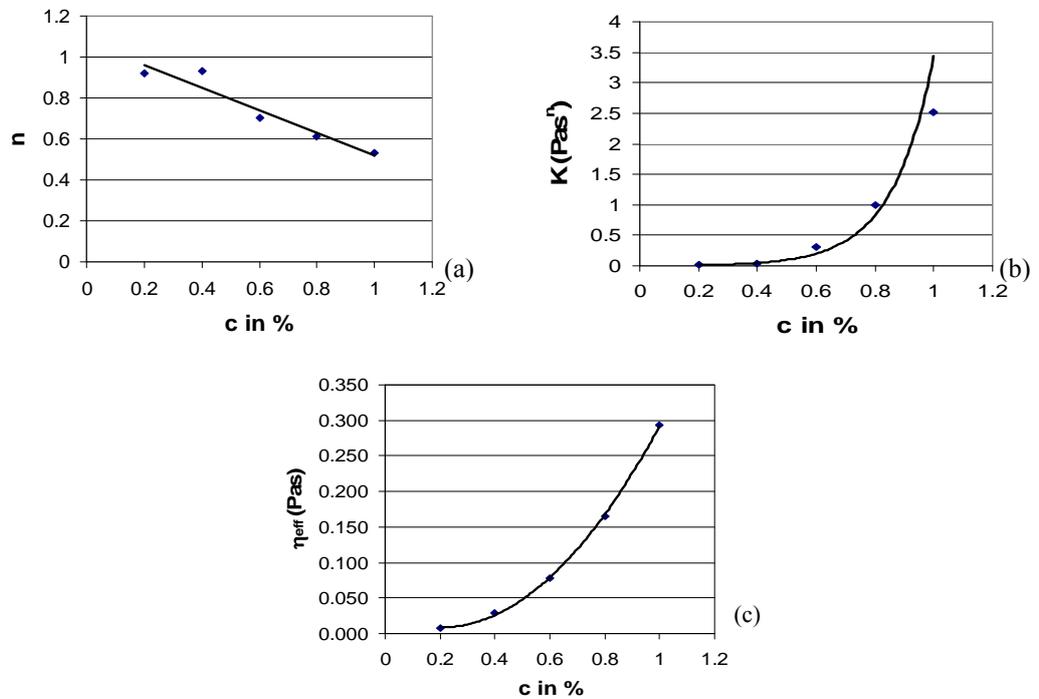


Figure 6.9 Trend line for rheological parameter prediction; flow index (a), consistency factor (b) and viscosity (c)

The Herschel-Bulkley and Ostwald-de Waele models were used for matching the curves and parameters. The results (Table 6.5) showed that yield point exhibited a negative value for Herschel-Bulkley model, so the Ostwald-de Waele model was used for describe the parameters. The flow index value (n) decreased with levels of concentration. Moreover, it was possible to predict the relationship of concentration and flow index (Figure 6.6). It could use the linear equation for predicting. (Eq 6.1) Thus, a high concentration produced the strong structure and high stability. Consistency factor (K) value also decreased with the concentration of locust bean gum. The trend of prediction curve (figure 6.6 b) could described by polynomial equation (Eq 6.2) In contrast, the viscosity increased with concentration. Particularly, the viscosity of concentration range from 0.6 to 1 % exhibited a rapidly increasing value. As can be seen on the viscosity trend curve (Figure 5.6 c), slope between concentration of 0.6 to 1 % was very shape. The equation of viscosity prediction was described by polynomial equation (Eq. 6.3). According to Figure 6.5, the diagram performed an increasing trend with shear rate. It can be described that locust bean gum performed non-Newtonian fluid behavior.

$$n(c) = -0.548 c_{\text{lb}g} + 1.069 \quad r = 0.959 \quad (\text{Eq 6.1})$$

$$K(c) = 6.0636 c_{\text{lb}g}^2 - 4.3015 \cdot c_{\text{lb}g} + 0.6846 \text{ in Pa}\cdot\text{s}^n \quad r = 0.991 \quad (\text{Eq 6.2})$$

$$\eta_{\text{eff}}(c) = 0.4467 c_{\text{lb}g}^2 - 0.1818 c_{\text{lb}g} + 0.0271 \text{ in Pa} \quad r = 0.999 \quad (\text{Eq 6.3})$$

*Validity: $0.1 \leq \dot{\gamma} \leq 1000/\text{s}$ and $0.2 \leq c_{\text{lb}g} \leq 1 \%$

Dolz *et al.* (2006) researched the influence of xanthan and locust bean gum upon flow and thixotropic behavior of food emulsion containing modified starch. Locust bean gum solution exhibited the shear thinning for lowest shear rates as well. This variation in viscosity with shear rate was well predicted by Ostwald-de Waele model, which most success model used in matching with our sample.

6.2.2 Effect of Temperature for locust bean gum on rheological properties

The effect of temperature on the rheological properties of LBG was investigated on temperature effect. The LBG was varied into five levels by using the concentration: 0.2, 0.4, 0.6, 0.8 and 1 %. The rheological properties of each level of concentration were measured using control shear rate examination by measuring at temperature of 20, 30, 40, 50 and 60 °C. The method of rheology was used the double gap set with 1 phase method. The shear rate was up to 1000/s. The diagrams and parameters were described by Ostwald-de Waele and Herschel-Bulkley model. The relationship between concentration and temperature was analyzed the statistic by using the Response surface methodology.

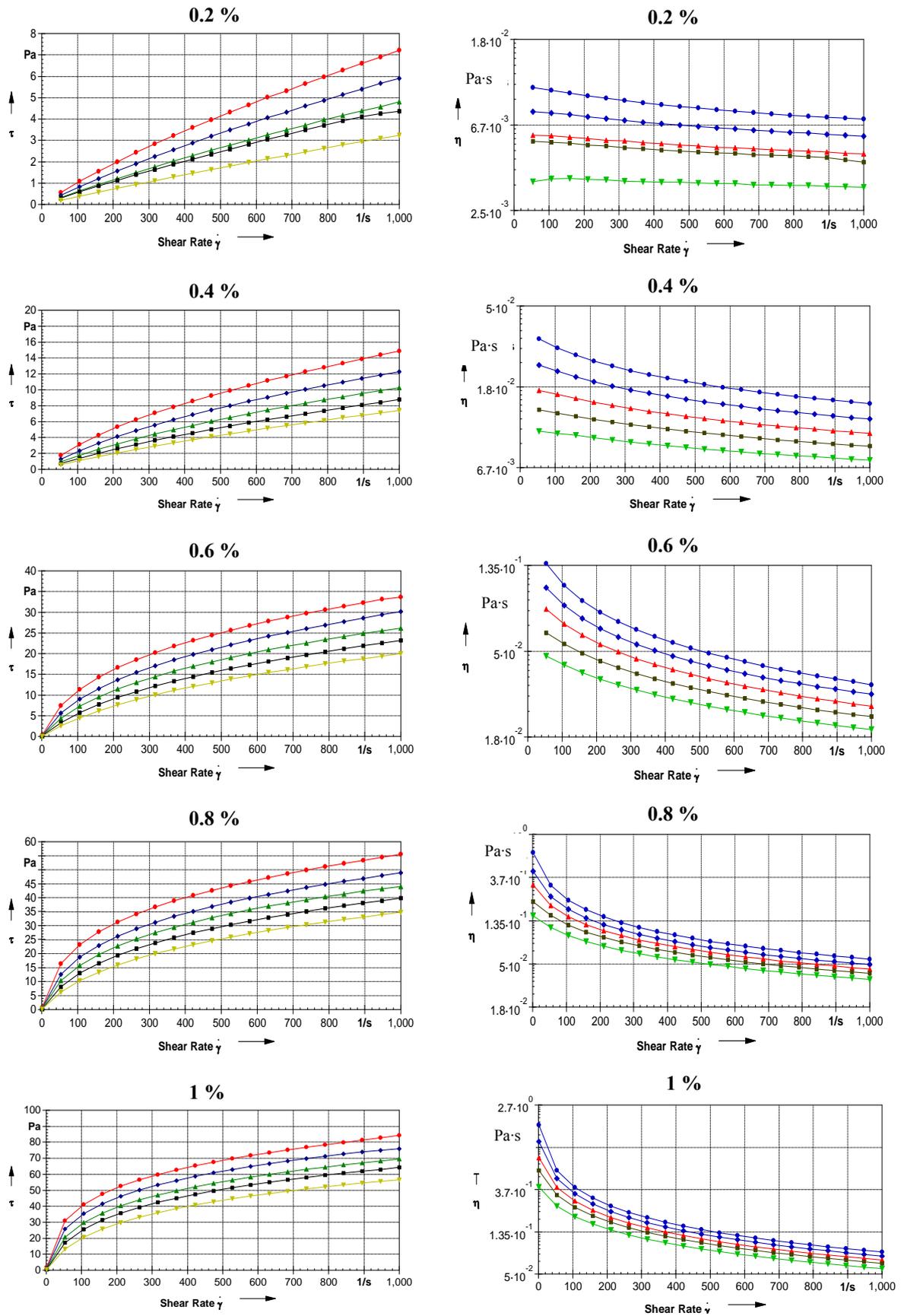


Figure 6.10 CRS Diagrams for locust bean gum solution at different concentration and temperature; 20°C (●), 30°C (◆), 40°C (▲), 50°C (■) and 60°C (▼)

Table 6.6 Rheological parameter of Ostwald equation for LBG on different temperature and concentration (1 phase; $0 < \dot{\gamma} < 1000$)

c %	t_{20}	t_{60}	ΔK (20-60 °C) $Pa \cdot s^n$	Δn (20-60 °C) -	$\Delta \eta_{eff}$ (1000/s) (20-60 °C) $Pa \cdot s$
0.2	OW	OW	0.0083	(-) 0.078	0.0068
	n : 0.921	n : 0.999			
	K : 0.013	K : 0.005			
	r : 0.986	r : 0.950			
0.4	OW	OW	0.0376	(-) 0.096	0.0151
	n : 0.845	n : 0.941			
	K : 0.0498	K : 0.0122			
	r : 0.971	r : 0.990			
0.6	OW	OW	0.258	(-) 0.167	0.0479
	n : 0.702	n : 0.869			
	K : 0.318	K : 0.060			
	r : 0.928	r : 0.940			
0.8	OW	OW	0.758	(-) 0.150	0.0901
	n : 0.611	n : 0.761			
	K : 0.978	K : 0.220			
	r : 0.911	r : 0.929			
1	OW	OW	1.916	(-) 0.156	0.1510
	n : 0.534	n : 0.690			
	K : 2.511	K : 0.595			
	r : 0.899	r : 0.900			
	$\eta_{eff} : 0.2937$	$\eta_{eff} : 0.1427$			

According to table 6.6, the influence of temperature on consistency factor (K) showed that K value decreased with temperature. It can be seen that the difference in the K value (ΔK) exhibited a positive value. Temperature has slightly influence on consistency factor. Temperature influence increased with concentration as can be seen the increasing of ΔK . However, the temperature was a high influence when the concentration was more than 0.8 %. The flow index was increased, with increasing in temperature as it can be seen by the negative value of difference of flow index value (Δn). Therefore, the structure of locust bran gum lost stability when temperature was higher. In the relationship between concentration and temperature on flow index, the influence of temperature was increased when concentration was increased. It can be seen that the Δn increased with concentration. The Δn value increased rapidly at a concentration of 0.6 %. Therefore, the structure of high concentration of LBG was weak and can be easily broken by shearing.

Concerning the effect of temperature and concentration, the viscosity was decreased with temperature as can be seen in the positive value of difference of viscosity ($\Delta \eta_{eff}$). It can be explained that the heating (or temperature) destroyed the structure and as a consequently, the viscosity decreased at condition of high heat. In the relationship between temperature and concentration, temperature has more influence when LBG has a higher concentration. It can be seen in the results that the $\Delta \eta_{eff}$ increased with concentration. This means that the LBG has a weak structure and is easy to break by temperature treatment. When temperature was increased, the non-Newtonian deviation was decreased.

The relationship between concentration and temperature with rheology parameters matched curves and the diagrams was created using the statistic program. (Statistica 7.0) The relationship trend between concentration and temperature on consistency factor is shown in RSM diagram (Figure 6.11) A highest K value was at 1 % of concentration with low temperature. (20 °C) On the other hand, the lowest of K value was at 0.2 % of concentration with low temperature. The prediction trend matched a Quadratic equation (Eq 6.4). The highest flow index value was at 1 % of concentration with high temperature (60 °C). The prediction trend matched the linear equation (Eq. 6.5). The highest of viscosity was at concentration of 1 % at temperature of 20 °C. A prediction curve matched a quadratic equation. (Eq. 6.6)

$$K(c, t) = 0.0328 - 0.251 \cdot c_{\text{lbG}} - 0.003 \cdot t + 3.4101 \cdot c_{\text{lbG}}^2 - 0.0554 \cdot c_{\text{lbG}} \cdot t + 0.0003 \cdot t^2$$

in Pa·sⁿ r = 0.822 (Eq 6.4)

$$n(c, t) = 0.9247 - 0.4397 \cdot c_{\text{lbG}} + 0.0031 \cdot t$$

r = 0.958 (Eq 6.5)

$$\eta_{\text{eff}}(c, t) = -0.0007 + 0.0064 \cdot c_{\text{lbG}} + (9.467 \cdot 10^{-5}) \cdot t + 0.03567 \cdot c_{\text{lbG}}^2 + 0.0045 \cdot c_{\text{lbG}} \cdot t + (1.334 \cdot 10^{-5}) t^2$$

in Pa·s r = 0.933 (Eq 6.6)

*Validity: $0.1 \leq \dot{\gamma} \leq 1000/\text{s}$ and $0.2 \leq c_{\text{lbG}} \leq 1\%$

In figure 6.11 showed the RSM plots of relationship between concentrations of LBG and temperature changing on rheological parameters, such as consistency factor, flow index and effective viscosity. The equation matched the diagram was chosen base on r value.

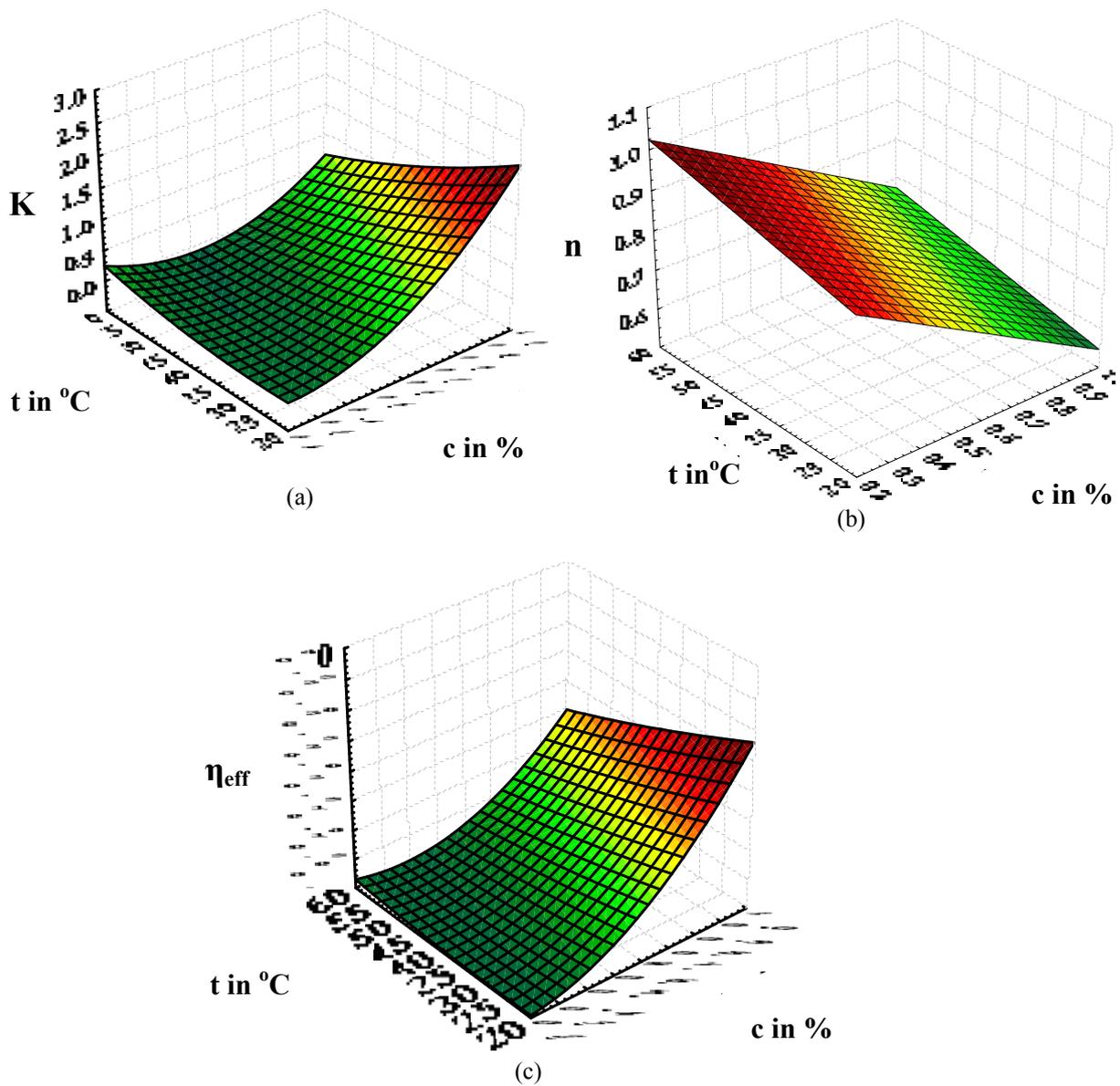


Figure 6.11 Response surface diagram for relationship between concentration and temperature on rheological parameters; Consistency factor (a), flow index (b) and viscosity (c)

Table 6.6 showed a Frenkel-Eyring equation which is used to describe the influence of temperature on appearance viscosity at shear rate of 1000/s. The activation energy (E_a) was decreased with concentration of LBG from 23000 kJ/mol at concentration of 0.2 % to 14376 kJ/mol at concentration of 1 %. Rao (1999) said that the quantity E_a is the energy barrier that must be overcome before the elementary flow process can occur. Therefore, the high concentration of locust bean gum used the less energy to overcome the barrier than low concentration.

Table 6.7 Flow activate energy for LBG solution

c %	Frenkel-Eyring Equation	r	E _a kJ/mol
0.2	$\ln\eta_{(T)} = 2766.5/T - 14.03$ $\eta(T) = 1244196 \exp(2766.5/T)$	0.844	23,000
0.4	$\ln\eta_{(T)} = 2330.2/T - 11.657$ $\eta(T) = 115497 \exp(2330.2/T)$	0.994	19,373
0.6	$\ln\eta_{(T)} = 2172.7/T - 9.9126$ $\eta(T) = 20170.98 \exp(2172.7/T)$	0.997	18,063
0.8	$\ln\eta_{(T)} = 1915.6/T - 8.3435$ $\eta(T) = 4209.08 \exp(1915.6/T)$	0.997	15,926
1	$\ln\eta_{(T)} = 1729.2x/T - 7.1116$ $\eta(T) = 4200.60 (\exp(1729.2/T))$	0.998	14,376

6.3 Rheological properties of guar gum

Guar gum is the one of stabilizers in the galactomannan group like locust bean gum, but the structure is slightly different with ratios of guar gum and locust bean gum of 1:2 and 1:4 respectively. In this study, the factor of guar gum, such as concentration and temperature was investigated on rheological properties. The rheological measurement was used the control shear examination method with five phase of measurement by using shear rate up to 50/s.

6.3.1 Effect of concentration of guar gum on rheological properties

To study the influence of concentration of guar on rheological properties, the concentration of guar gum was varied at 0.2, 0.4, 0.6, 0.8 and 1 %. The pH of guar gum was adjusted to 3.5 at all of samples. Results were analyzed by matching the Herschel-Bulkley and the Ostwald-de Waele models. The rheology parameters were calculated on the fifth phase or down curve, because the structure was steady on this phase. Table 6.12 showed the CSR-examination; shear stress versus shear rate, viscosity and shear rate on guar gum concentration effect.

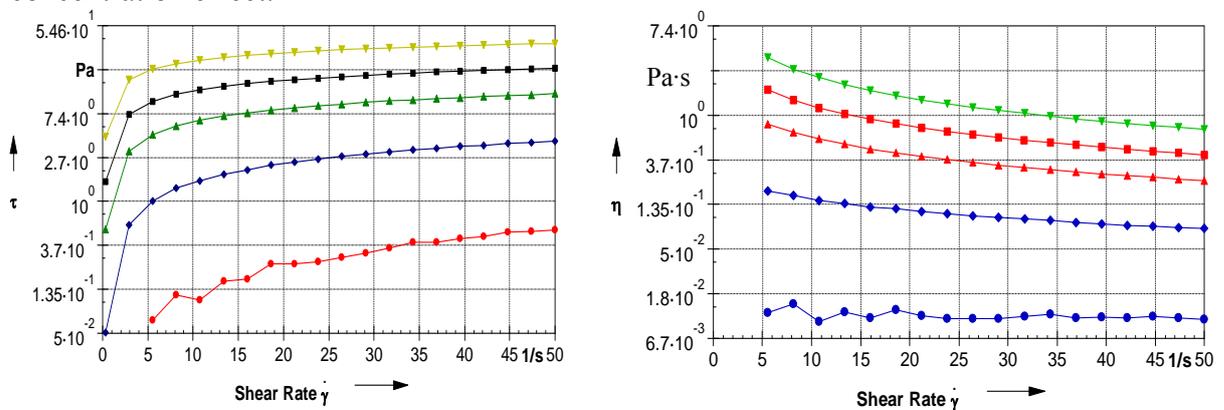


Fig 6.12 CSR-Examiantion of shear rate examination on guar gum in different concentration; 0.2 % (●), 0.4 % (◆), 0.6 % (▲), 0.8 % (■) and 1 % (▼)

Table 6.8 showed rheological parameter of Herschel-Bulkley and Ostwald-de Waele models on different concentration of guar gum solution at 20 °C. The concentration of guar gum varied from 0.2, 0.4, 0.6, 0.8 and 1 %. This table also showed the validation of model on concentration effect.

Table 6.8 Rheological parameters for the concentration of guar gum solution at 20 °C

<i>c</i> %	<i>OW</i>					<i>HB</i>					
	K Pa·s ⁿ	n -	r -	η_{eff} (50/s) Pa·s	τ_0 Pa	K Pa·s ⁿ	n -	r	A_{TH} Pa/s	η_{eff} (50/s) Pa·s	
0.2	0.01	0.970	0.967	0.016	√ -0.06	0.03	0.698	0.993	0.19	0.009	-
0.4	0.20	0.901	0.960	0.127	√ -0.16	0.42	0.585	0.998	0.89	0.062	-
0.6	1.44	0.560	0.965	0.191	√ -1.74	3.52	0.344	0.999	5.47	0.155	-
0.8	3.69	0.468	0.963	0.319	√ -7.16	11.47	0.228	0.999	6.36	0.256	-
1	9.02	0.382	0.959	0.524	√ -34.22	44.47	0.119	0.999	13.67	0.427	-

Results showed that rheology parameter (Table 6.7) matched Herschel-Bulkley and Ostwald de-Weale model base on the r value consideration. ($r > 0.950$) However, yield point (τ_0) in the Herschel-Bulkley model exhibited a negative value. The best model for matching the parameters and curves on the effect of concentration was the Ostwald-de Waele model. From results at table 6.7, the consistency facto (K) increased with concentration. Flow index decreased with increasing concentration. Therefore, the structure of guar gum was strong and performed more stability at high concentration. The viscosity of guar gum increased logically with concentration from 0.009 Pa·s at concentration of 0.2 % to 0.427 Pa·s at concentration of 1 %. According to yield point showed a more negative value and flow index decreased with concentration. It can be described that the guar gum performed more property as particle dispersion when concentration was high.

In figure 6.13 showed predicted curves of rheological parameters, such as consistency factor, flow index and effective viscosity. This curves and equation validated between concentration of 0.2 to 1 % and shear rate between 0.1 to 1/s.

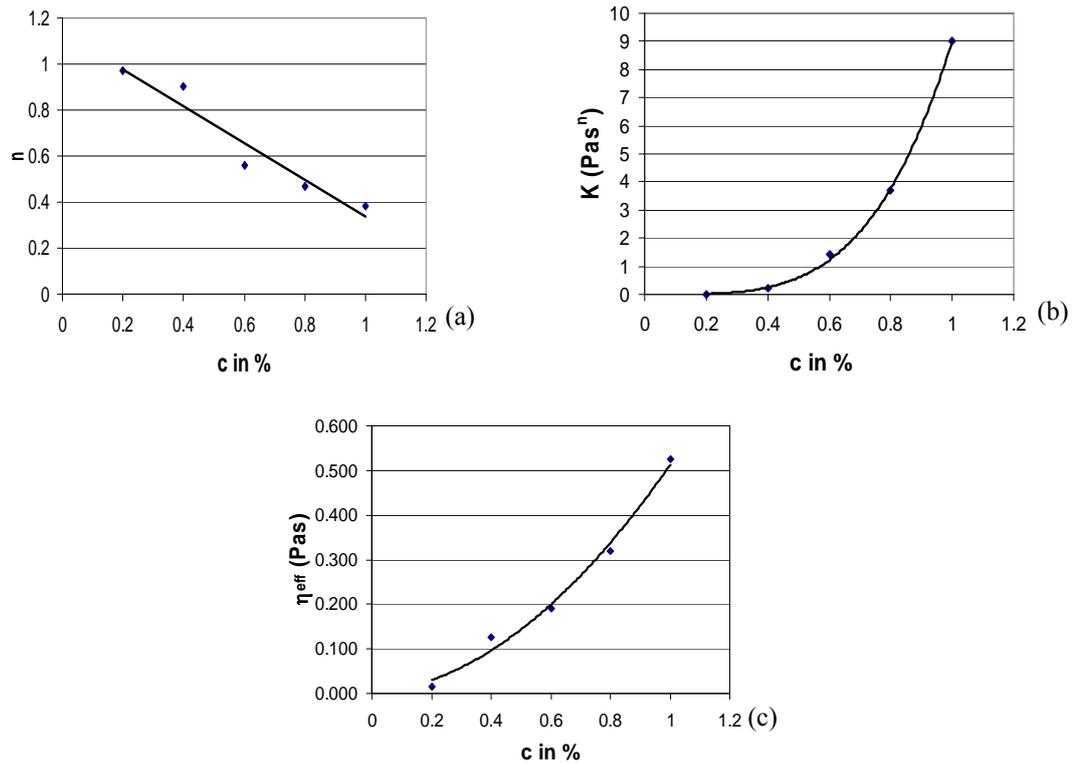


Figure 6.13 Trend line for rheological parameter prediction for guar gum; flow index (a), consistency factor (b) and viscosity (c)

Figure 6.13 showed the predicted trend of parameters for guar gum concentration. The flow index decreased with concentration. The trend line matched a linear equation. (Eq. 6.7) The consistency factor exhibited an increasing trend with concentration. The trend line matched a polynomial equation. (Eq. 6.8) For the prediction of viscosity on concentration factor, the viscosity line showed the increasing trend with concentration. The predicted trend matched a polynomial equation. (Eq. 6.9)

$$n(c) = -0.8045 \cdot c_{gg} + 1.1389 \quad r = 0.930 \quad (\text{Eq. 6.7})$$

$$K(c) = 20.177 \cdot c_{gg}^2 - 13.454 \cdot c_{gg} + 2.0728 \text{ in Pa} \cdot \text{s}^n \quad r = 0.991 \quad (\text{Eq. 6.8})$$

$$\eta_{\text{eff}}(c) = 0.4499 \cdot c_{gg}^2 + 0.0646 \cdot c_{gg} - 0.0013 \text{ in Pa} \cdot \text{s} \quad r = 0.988 \quad (\text{Eq. 6.9})$$

*Validity: $0.1 \leq \dot{\gamma} \leq 50/\text{s}$ and $0.2 \leq c_{gg} \leq 1\%$

6.3.2 Effect of temperature on guar gum solution

The temperature was the one of important factor for rheological properties changing of guar gum. To study the temperature effect on guar gum solution, the guar gum at different concentration (0.2, 0.4, 0.6, 0.8 and 1 %) was measured the rheology at five level of temperature, such as 20, 30, 40, 50 and 60 °C. The rheological properties were measured by using the control shear rate examination ($0 \leq \dot{\gamma} \leq 50/\text{s}$) with five phases of measurement. The parameters were calculated from fifth phase of diagrams. The relationship of

concentration and temperature described different value of parameters between low and high temperature. The parameters were predicted by using RSM diagrams.

Table 6.9 showed the different of rheological parameters, such as consistency factor, flow index and effective viscosity, between temperature of 20 and 60 °C on different concentration of guar gum solution, such as 0.2, 0.4, 0.6, 0.8 and 1%.

Table 6.9 Rheological parameters of guar gum at different temperature and concentration

<i>c</i> %		<i>t</i> ₂₀	<i>t</i> ₆₀	ΔK (20-60 °C) Pa·s ⁿ	Δn (20-60 °C) -	$\Delta \eta_{eff}$ (50/s) (20-60 °C) Pa·s
0.2	OW	n : 0.970	OW	0.013	(-) 0.03	0.010
		K : 0.018	n : 1.000			
		r : 0.967	K : 0.005			
		η_{eff} : 0.015	r : 0.980			
0.4	OW	n : 0.901	OW	0.15	(-) 0.098	0.043
		K : 0.201	n : 0.999			
		r : 0.96	K : 0.051			
		η_{eff} : 0.127	r : 0.959			
0.6	OW	n : 0.560	OW	0.961	(-) 0.179	0.209
		K : 1.447	n : 0.739			
		r : 0.965	K : 0.486			
		η_{eff} : 0.190	r : 0.963			
0.8	OW	n : 0.468	OW	1.989	(-) 0.136	0.201
		K : 3.698	n : 0.604			
		r : 0.963	K : 1.709			
		η_{eff} : 0.319	r : 0.963			
1	OW	n : 0.382	OW	4.956	(-) 0.142	0.314
		K : 9.028	n : 0.524			
		r : 0.959	K : 4.072			
		η_{eff} : 0.524	r : 0.955			
						η_{eff} : 0.454

Figure 6.14 showed the rheological diagram between shear stress versus shear rate, effective viscosity versus shear rate at different temperature (20 - 60 °C) on different concentration of guar gum. (0.2 - 1 %) Those diagrams described by Herschel Bulkley and Ostwald-de Waele models on table 6.9.

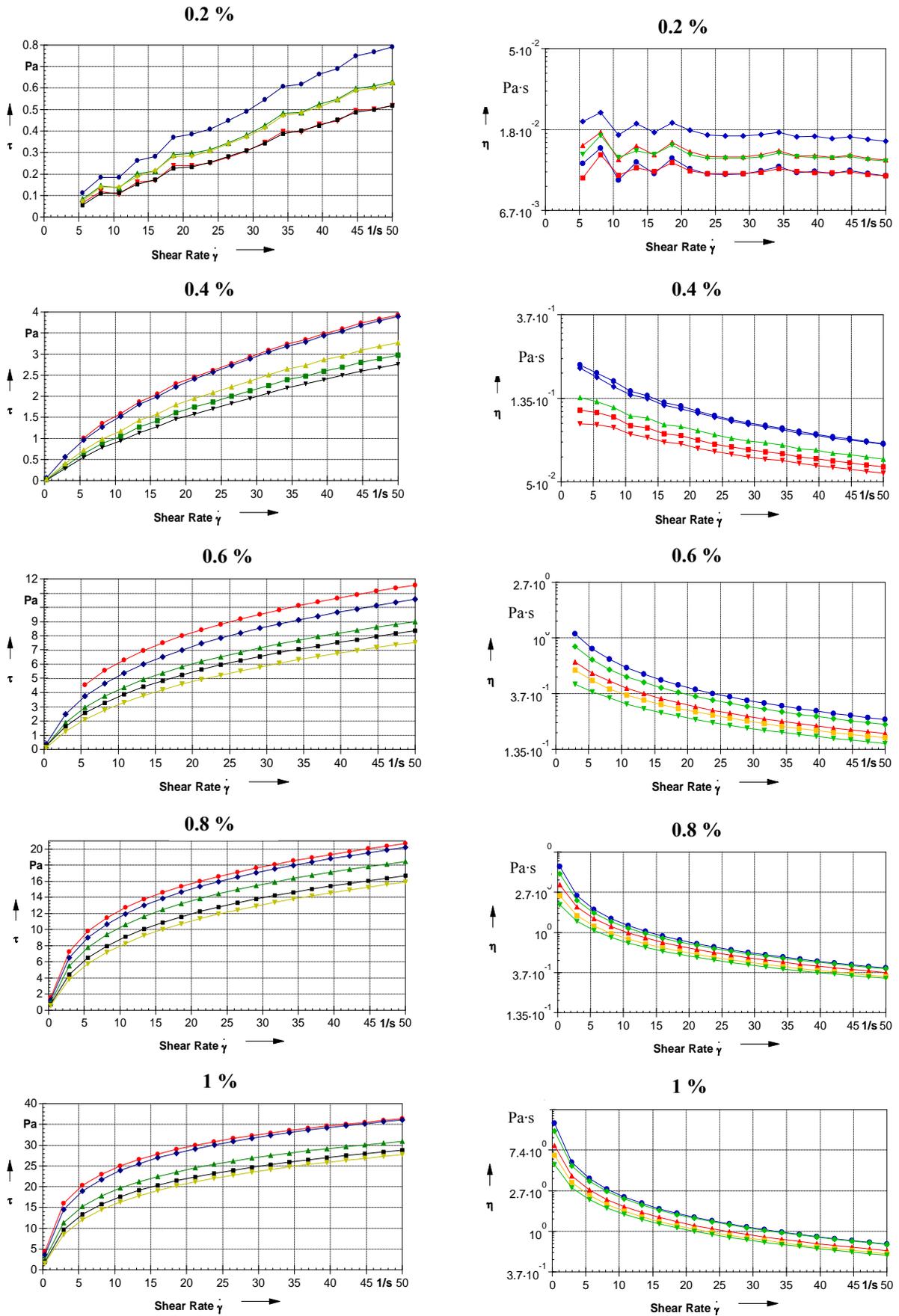


Figure 6.14 CRS-Examinations for guar gum solution at different concentration and temperature; 20 °C (●), 30 °C (◆), 40 °C (▲), 50 °C (■) and 60 °C (▼)

Results in table 6.9 showed the effect of temperature on the structure of guar gum. The rheological parameters matched the Ostwald-de Waele model closely at all range of temperature and concentration. The difference in the consistency factor (ΔK) showed a positive value at every level of concentration and increased with concentration. This indicate that at given guar gum concentration, increasing the temperature could decrease the consistency of guar gum. The effect of concentration is more pronounced if the concentration is higher than 0.4%. For flow index (n), the difference in the flow index parameter (Δn) showed a negative value and decreased with an increasing concentration. Therefore, the flow index decreased with temperature. The concentration has more influence when the concentration of guar gum is high than when it was low. This was because the structure of guar gum was destroyed by temperature.

The difference in the viscosity showed a positive value and increased with concentration. The viscosity of guar at low temperature was higher than its viscosity at high temperature. It can be confirmed that the explanation shown by flow index result. The structure of guar gum was destroyed by temperature changing, so the viscosity of guar gum was less when temperature increasing. The relationship between concentration and temperature on guar gum viscosity showed that temperature has more influence with high concentration than low concentration of guar gum.

Patel *et al* (1987) investigated the rheological properties of guar gum and hydroxyl guar gum in aqueous solution. They found that guar gum exhibited pseudoplastic without yield point over the range of temperature from 30 to 60 °C. This was the same as our results: the viscosity was decreased with shear rate and temperature. This behavior was also called “non-Newtonian fluid behavior”.

As shown in figure 6.15, the trends of parameters were exhibited in the RSM diagrams between concentration and temperature. For the consistency factor (K), the highest value of K on the prediction trend was at concentration of 1 % and temperature of 20 °C. The prediction trend matched the quadratic equation (Eq. 6.10) The highest flow index value was at a concentration of 0.2 % and temperature of 60 °C. The prediction trend matched the quadratic equation. (Eq. 6.11) The highest viscosity value was at concentration of 1 % and temperature of 20 °C. The lowest viscosity was at concentration of 0.2 % and temperature of 60 °C. The prediction trend matched the quadratic equation (Eq. 6.12).

$$K(c,t) = 0.0462 - 3.6784 \cdot c_{gg} + 0.0191 \cdot t + 14.4814 \cdot c_{gg}^2 - 0.1527 \cdot c_{gg} \cdot t + 0.0004 \cdot t^2$$

in Pa·sⁿ r = 0.974 (Eq 6.10)

$$n(c,t) = 1.1674 - 1.0806 \cdot c_{gg} + 0.0009 \cdot t + 0.1821 \cdot c_{gg}^2 + 0.0031 \cdot c_{gg} \cdot t + (1.1429 \cdot 10^{-6}) \cdot t^2$$

r = 0.949 (Eq 6.11)

$$\eta_{eff}(c,t) = 0.0311 + 0.0478 \cdot c_{gg} - 0.0013 \cdot t + 0.4994 \cdot c_{gg}^2 - 0.0015 \cdot c_{gg} \cdot t + (9.3261 \cdot 10^{-6}) \cdot t^2$$

in Pa·s r = 0.945 (Eq 6.12)

*Validity: $0.1 \leq \dot{\gamma} \leq 50/s$ and $0.2 \leq c_{gg} \leq 1 \%$

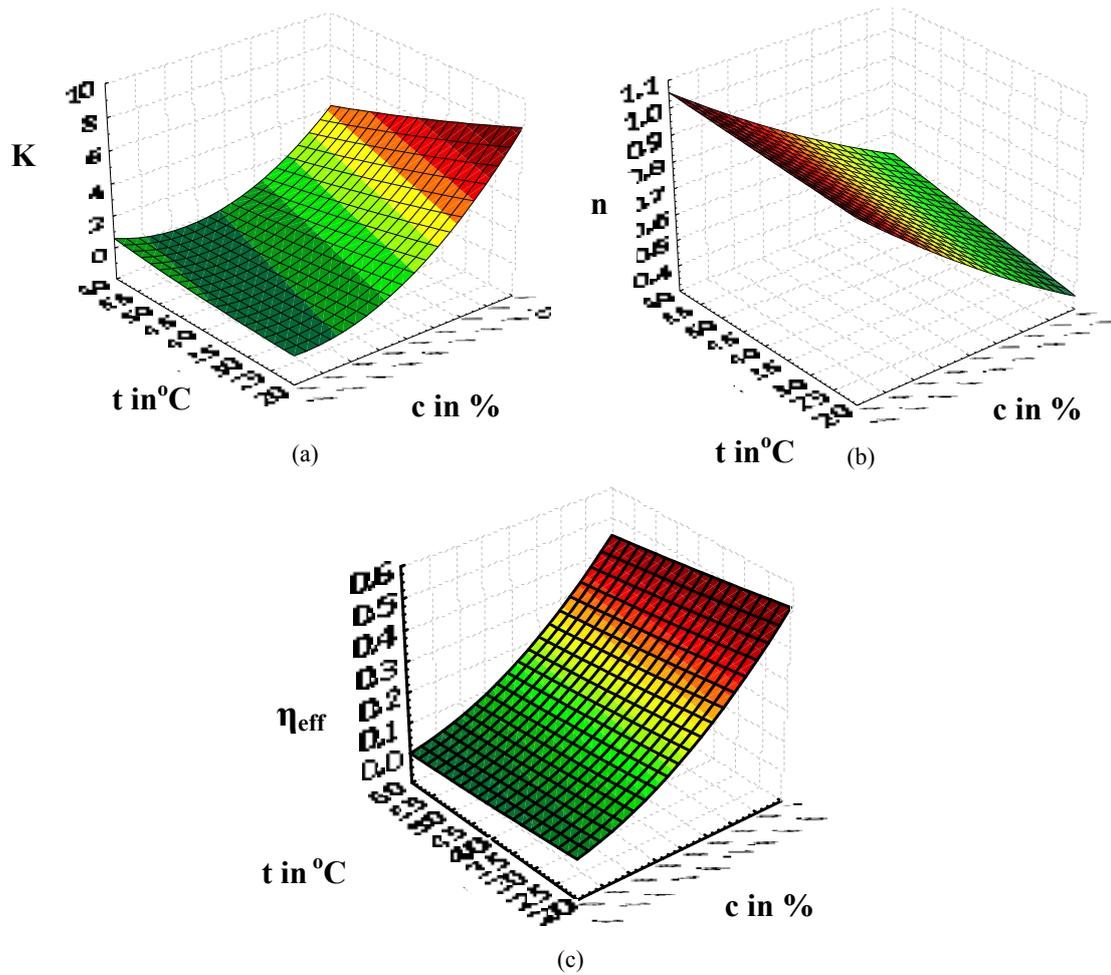


Figure 6.15 Response surface diagram for relationship between concentration and temperature on rheological parameters of guar gum; Consistency factor (a), flow index (b) and viscosity (c)

Table 6.9 showed that the activation energy of temperature change for guar gum. The flow activate energy or E_a decreased with concentration of guar gum, so the energy used for flow behavior at high concentration of guar gum between temperature of 20 °C to 60 °C was less than at low concentration. Patel (1987) showed the same result as our results: the E_a decreased with concentration. However, the guar gum has been measured on temperature range from 30 to 60 °C.

Table 6.10 Flow activate energy for temperature changing of guar gum solution

C %	Frenkel-Eyring Equation	r	E _a kJ/mol
0.2	$\ln\eta_{(T)} = 2656.9/T - 13.307$ $\eta(T) = 1.7 \cdot 10^{-7} \exp(2656.9/T)$	0.974	22,089
0.4	$\ln\eta_{(T)} = 2554.5/T - 10.717$ $\eta(T) = 2.2 \cdot 10^{-6} \exp(2554.5/T)$	0.961	21,238
0.6	$\ln\eta_{(T)} = 716.1/T - 4.0921$ $\eta(T) = 0.0167 \exp(716.1/T)$	0.983	5,953
0.8	$\ln\eta_{(T)} = 412.17/T - 2.5255$ $\eta(T) = 0.08 \exp(412.17/T)$	0.95	3,426
1	$\ln\eta_{(T)} = 434.05/T - 2.1061$ $\eta(T) = 0.1217 \exp(434.05/T)$	0.913	3,608

6.4 Rheological properties of xanthan gum

Xanthan gum was the one of animal gum was used as stabilizer in several products. The stabilizers have rheological properties to consider for important identification of uses, such as stability or viscosity. The concentration of xanthan gum and temperature influence were analyzed by using the rheological methods: shear rate examination with one phase of measurement. ($0 \leq \dot{\gamma} \leq 1000/s$) The aim of this study was to investigate the rheological properties of xanthan gum on effect of concentration and temperature before its use in pineapple puree in next examination.

6.4.1 Effect of concentration on xanthan solution

To study the effect of concentrations of xanthan solution on rheological properties, xanthan gum, different levels of concentration were prepared: at 0.2, 0.4, 0.6, 0.8 and 1 %. The rheological parameters were analyzed by using the Herschel-Bulkley and Ostwald-de Waele models. Table 6.16 showed the rheological diagrams between shear stress versus shear rate and effective viscosity versus shear rate on xanthan gum solution at different concentration; 0.2, 0.4, 0.6, 0.8 and 1 %.

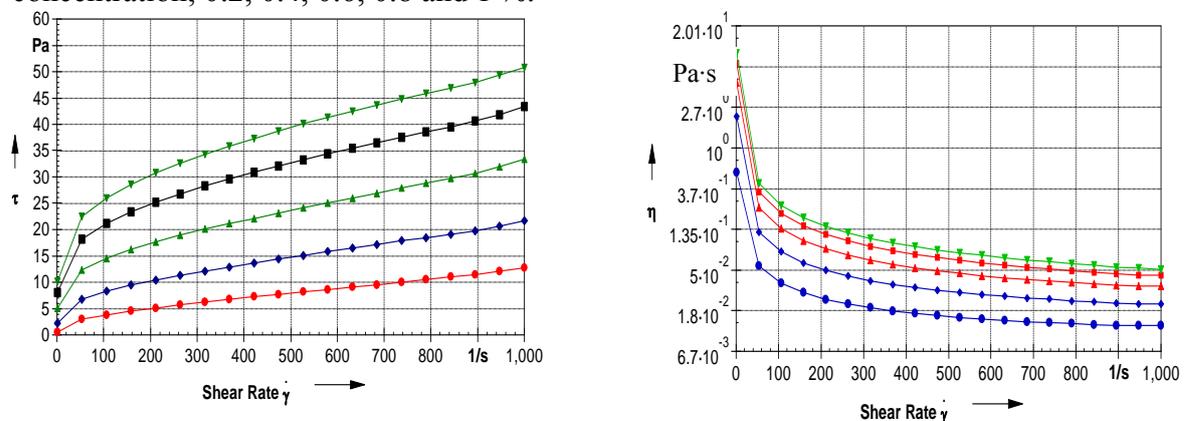


Fig 6.16 CSR-Examinations of shear rate on xanthan gum in different concentration; 0.2 % (●), 0.4 % (◆), 0.6 % (▲), 0.8 % (■) and 1 % (▼)

In Table 6.11 show rheological parameters of Herschel Bulkley and Ostwald-de Waele models on xanthan solution at different concentration, such as 0.2, 0.4, 0.6, 0.8 and 1 %.

Table 6.11 Rheological parameters for concentration of xanthan gum solution

c %	<i>OW</i>					<i>HB</i>					
	K Pa·s ⁿ	n -	r -	η_{eff} (1000/s) Pa·s	τ_0 Pa	K Pa·s ⁿ	n -	r -	η_{eff} (1000/s) Pa·s		
0.2	0.493	0.451	0.984	0.011	-	0.272	0.279	0.537	0.940	0.012	√
0.4	1.896	0.333	0.978	0.019	-	1.434	0.751	0.466	0.978	0.020	√
0.6	4.400	0.278	0.949	0.030	-	3.627	1.435	0.428	0.990	0.031	√
0.8	7.214	0.245	0.981	0.039	-	5.515	2.566	0.382	0.997	0.041	√
1	9.281	0.264	0.985	0.057	-	6.708	3.545	0.359	0.998	0.049	√

Results showed that rheological parameters (Figure 6.16) matched the Herschel-Bulkley and Ostwald-de Waele models base on high value of r parameter. However, the xanthan solution was showed a positive value of yield point, so the yield point was considered in calculate as parameters. Therefore, the parameters and curve fitted with Herschel Bulkley models better than the Ostwald-de Waele model. Base on the Herschel Bulkley model, consistency factor (K) increased with concentration. The flow index (n) decreased with concentration. Therefore, the structure of xanthan at high concentration was more stable than xanthan gum at low concentration. The viscosity of xanthan gum also increased with concentration, but the viscosity was only slightly increased. Marcotte *et al.* (2001) studied the rheological properties of selected hydrocolloids, such as xanthan gum, pectin. The properties of xanthan gum solution showed a result the same as our. The parameter of xanthan gum solution matched the Herschel-Bulkley model, because of the positive value of yield point. Moreover, the flow index value decreased with concentration. The results demonstrated that the xanthan gum showed the good properties as a stabilizer, because xanthan gum did not produced high viscosity. In contrast the structure was strong, when concentration increased.

In Figure 6.17 show predicted curved of rheological parameters, such as consistency factor, flow index and effective viscosity. Each curve has the equation for predicting the parameters value. The curve and equation validated at concentration of 0.2 to 1 % and at shear rate of 0.1 to 1000/s.

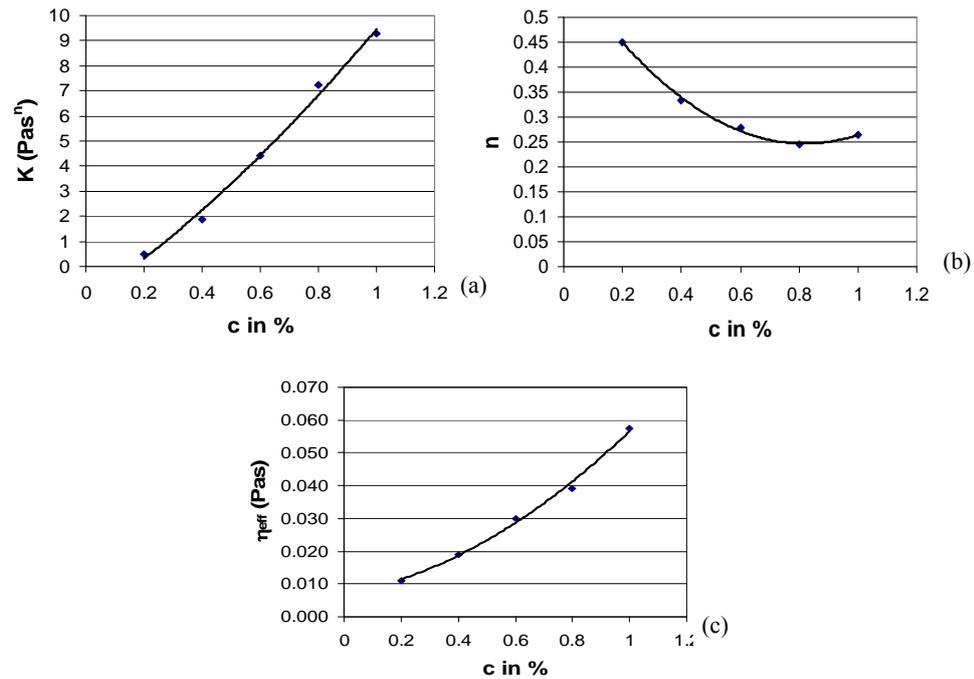


Figure 6.17 Trend line for rheological parameter prediction for xanthan gum; flow index (a), consistency factor (b) and viscosity (c)

Trends of concentration effect are shown in figure 6.17. The consistency factor showed an increased with concentration. The trend diagram matched the polynomial equation. (Eq. 6.13) The flow index diagram showed a decreasing trend with an increase in concentration. The trend curve matched the polynomial equation. (Eq. 6.14) The viscosity trend showed an increasing trend with concentration. The trend diagram matched the polynomial equation. (Eq. 6.15).

$$K(c) = 2.925 \cdot c_{xg}^2 + 7.937 \cdot c_{xg} - 1.3924 \quad \text{in Pa} \cdot \text{s}^n \quad r = 0.996 \quad (\text{Eq. 6.13})$$

$$n(c) = 0.5286 \cdot c_{xg}^2 - 0.8653 \cdot c_{xg} + 0.6008 \quad r = 0.998 \quad (\text{Eq. 6.14})$$

$$\eta_{\text{eff}}(c) = 0.034 \cdot c_{xg}^2 + 0.0157 \cdot c_{xg} + 0.007 \quad \text{in Pa} \cdot \text{s} \quad r = 0.996 \quad (\text{Eq. 6.15})$$

*Validity: $0.1 \leq \dot{\gamma} \leq 1000/\text{s}$ and $0.2 \leq c_{xg} \leq 1\%$

6.4.2 Effect of temperature on xanthan solution

To study effect of temperature on xanthan gum solution, the rheological properties of xanthan gum at different concentration (0.2, 0.4, 0.6, 0.8 and 1 %) was measured at temperature from 20, 30, 40, 50 and 60 °C. The aim of this study was to investigate the temperature effect on xanthan gum and study the relationship between concentration and temperature on rheological properties of xanthan gum solution. The rheological method was used the control shear rate examination. Figure 6.18 showed rheological diagrams of xanthan gum at different concentration: 0.2, 0.4, 0.6, 0.8 and 1 % on different temperature of measurement. (20 - 60 °C)

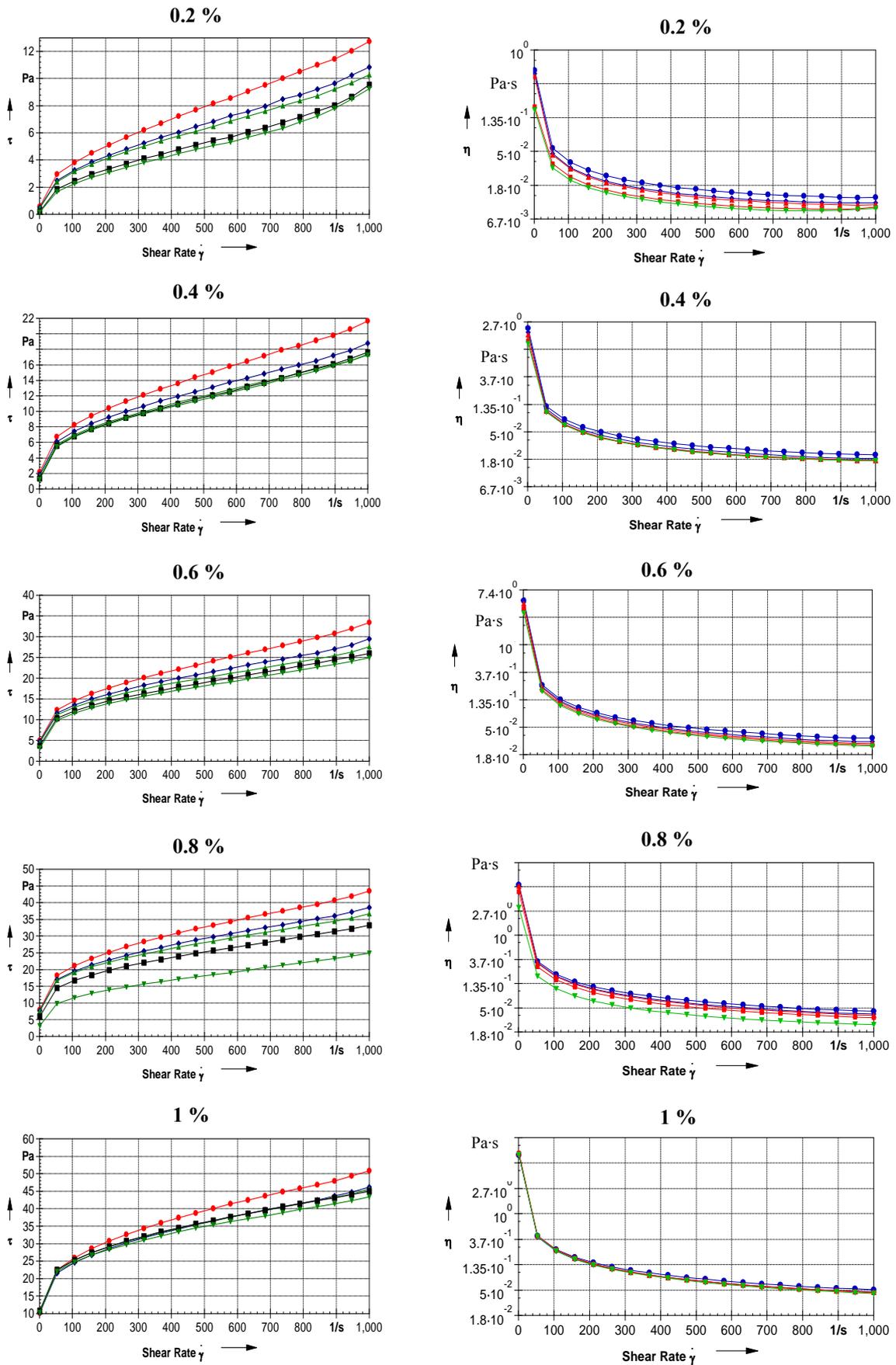


Figure 6.18 CRS-Examinations for xanthan gum solution at different concentration and temperature; 20 °C (●), 30 °C (◆), 40 °C (▲), 50 °C (■) and 60 °C (▼)

0.4) This was because the high concentration was lost stability more than the low concentration. The difference in viscosity ($\Delta\eta_{\text{eff}}$) showed the increasing potential with concentration. However, $\Delta\eta_{\text{eff}}$ value was reduced when xanthan solution at 1 %. Thus, the temperature has the greatest influence at 0.8 % of xanthan gum.

Trends of parameters for relationship between concentration and temperature are in figure 6.19. Results showed that the highest level of consistency factor trend was at 1 % of concentration and temperature of 60 °C. The trend matched the Quadratic equation (Eq. 6.16) The lowest value of flow index was at concentration of 1 % and temperature of 60 °C. The trend matched the Quadratic equation. (Eq. 6.17) The viscosity of xanthan showed an increasing trend with temperature and concentration. The highest value of viscosity was at concentration of 1 % and temperature of 20 °C. The predicted trend matched the linear equation. (Eq. 6.18)

$$K(c_{\text{xg}}, t) = 0.574 - 0.1777 \cdot c_{\text{xg}} - 0.0268 \cdot t + 2.8114 c_{\text{xg}}^2 + 0.0397 c_{\text{xg}} \cdot t + 0.0002 \cdot t^2$$

in Pa·sⁿ r = 0.996 (Eq. 6.16)

$$n(c_{\text{xg}}, t) = 0.6741 - 0.5567 c_{\text{xg}} - 0.0017 \cdot t + 0.3346 c_{\text{xg}}^2 - 0.0026 c_{\text{xg}} \cdot t + (2.82 \cdot 10^{-5}) t^2$$

r = 0.994 (Eq. 6.17)

$$\eta_{\text{eff}}(c_{\text{xg}}, t) = 0.0063 + 0.0444 c_{\text{xg}} - 0.0002 \cdot t \text{ in Pa} \quad r = 0.952 \quad (\text{Eq. 6.18})$$

*Validity: $0.1 \leq \dot{\gamma} \leq 1000/\text{s}$ and $0.2 \leq c \leq 1 \%$

Figure 6.19 showed RSM plots of relationship between concentration of xanthan solution and temperature of xanthan gum on rheological parameters changing, such as consistency factor, flow index and viscosity. The RSM also used for predicting the parameters by using the equation. The RSM plots validated at concentration of 0.2 to 1 %, temperature of 20 to 60 °C and shear rate of 0.1 to 1000/s.

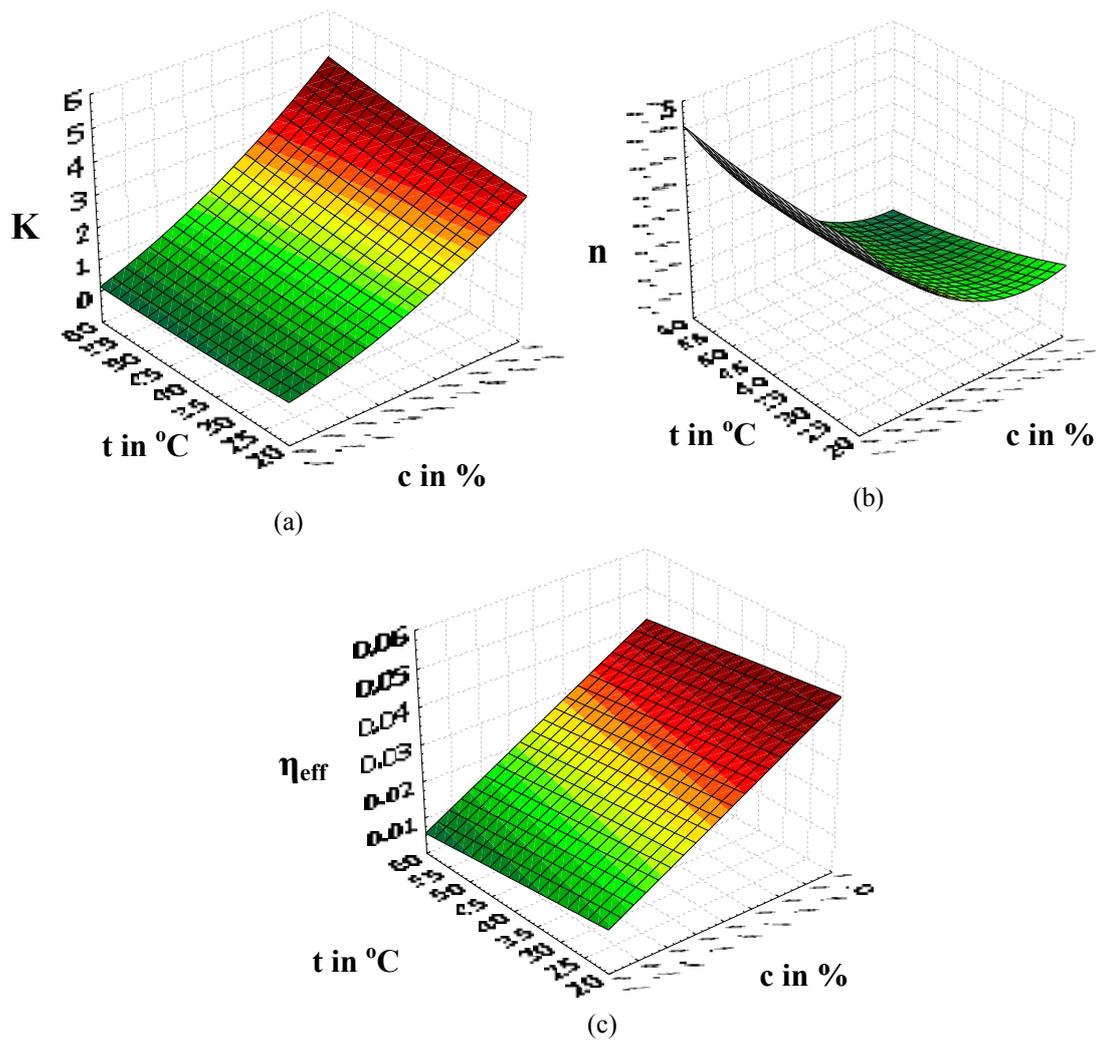


Figure 6.19 Response surface diagram for relationship between concentration and temperature on rheological parameters of xanthan gum; Consistency factor (a), flow index (b) and viscosity (c)

According to table 6.13, the flow activate energy of xanthan gum solution decreased with increasing concentration. Marcotte *et al.* (2001) studied the rheological properties of xanthan gum at different concentration (1-3 %) and different temperature (20 to 60 °C). The results showed the same trend as our results that the E_a was decreased with concentration.

Table 6.13 Flow activate energy for temperature changing of xanthan gum solution

c %	Frenkel-Eyring Equation	r	E _a kJ/mol
0.2	$\ln\eta_{(T)} = 1007.7/T - 7.9113$ $\eta(T) = 0.000367 \exp(1007.7/T)$	0.984	8,378
0.4	$\ln\eta_{(T)} = 564.7/T - 5.8752$ $\eta(T) = 0.002809 \exp(564.7/T)$	0.909	4,694
0.6	$\ln\eta_{(T)} = 677.59/T - 5.8093$ $\eta(T) = 0.003 \exp(677.59/T)$	0.973	5,633
0.8	$\ln\eta_{(T)} = 694.01/T - 5.5629$ $\eta(T) = 0.003841 \exp(694.01/T)$	0.953	5,321
1	$\ln\eta_{(T)} = 327.68/T - 4.1627$ $\eta(T) = 0.015565 \exp(327.68/T)$	0.892	2,724

6.5 Interaction between galactomannan and xanthan gum on rheological properties

Normally, galactomannan and xanthan gum have a strong interaction and exhibited a synergistic system. The characteristic of gum after mixing caused change in its rheological properties, such as stability, viscosity and viscoelasticity. The aim of this study was to investigate the effect of the galactomannan fraction of gum mixing solution on rheological properties. The galactomannan was mixed with xanthan gum in different ratio (galactomannan/xanthan): 100:0, 75:25, 50:50, 25:75, and 0:100. The total concentration of mixing gum was 1 %. Rheological measurement was used the control shear rate examination and the oscillation test. (Frequency sweep)

6.5.1 Shear rate examination

The shear rate examination was used the shear rate up to 1000/s with one phase of measurement. Rheological parameters matched the Hershel-Bulkley and the Ostwald-de Waele models. Table 6.14 showed rheological parameters of gum mixing solution between guar in xanthan gum and LBG in xanthan gum. This table report only valid model on each ratio of mixing gum: 100:0, 75:25, 50:50, 25:75 and 0:100.

Table 6.14 Rheological parameters for interaction between galactomannan and xanthan gum at 20 °C.

Ratio	GG/XG						LBG/XG					
	τ_0 Pa	K Pa·s ⁿ	n -	r -	η_{eff} (50/s) Pa·s	valid	τ_0 Pa	K Pa·s ⁿ	n -	r	η_{eff} (50/s) Pa·s	valid
100 : 0	-	9.028	0.382	0.959	0.524	OW	-	2.511	0.534	0.899	0.100	OW
75 : 25	-	13.81	0.251	0.998	0.078	OW	-	24.57	0.319	0.710	0.223	OW
50 : 50	2.24	9.821	0.264	0.998	0.063	HB	32.89	6.56	0.523	0.744	0.276	HB
25 : 75	5.56	6.519	0.229	0.998	0.037	HB	38.34	10.79	0.517	0.933	0.422	HB
0 : 100	6.70	3.545	0.359	0.998	0.049	HB	6.708	3.545	0.359	0.998	0.049	HB

Results (Table 6.14) showed that the parameters of galactomannan fraction at less than 50 % matched Ostwald-de Waele model. At level above 50 % of galactomannan fraction, the parameters matched the Herschel-Bulkley model. That was because the yield point of solution at less than 50 % exhibited negative value. It changed to positive value after the galactomannan fraction was equal to or higher than 50 %. It can be explained that the behavior of gum mixing galactomannan and xanthan gum solution was changed from fluid to non-Newtonian fluid behavior when the galactomannan fraction was higher than 50 % or equal. ($\geq 50\%$)

Interaction between guar gum and xanthan gum showed that the consistency factor decreased with an increasing in the galactomannan fraction. The guar gum solution showed the high value of viscosity, but stability properties was low. This was because the flow index value was high. The xanthan gum solution also exhibited a high value of flow index value compared with mixing gums solution and had a low viscosity value. In contrast, the mixed showed the lower flow index value than the pure gum solution and exhibited the low viscosity as xanthan gum. It can be described that the synergistic between guar gum and xanthan gum was able to improve the stability of solution very well. The best ratio of guar and xanthan gum for stability improvement was 25:75, which was about 0.229, but the viscosity didn't enhance very well.

Interaction between locust bean gum and xanthan gum showed that the viscosity of mixed gums solution increased significantly compared with pure gum solution. The viscosity increased significantly at ratio (LBG: XG) of 25:75 at 0.422 Pa·s. The stability of gums solution was improved significantly at ratio of 75:25 (LBG: XG) compare with other ratios because the flow index value decreased to 0.319. The combination between LBG and xanthan at ratios of 50: 50 and 25:75 showed the gel behaviors that give the high value yield point.

To comparing the interaction between the mixing gum solution of LBG with xanthan gum, and guar gum with xanthan gum, the combination between guar and xanthan gum was able to improve the stability better than LBG and xanthan gum. However, the guar gum combination could not to enhance the viscosity as good as LBG. Moreover, the combination between LBG and xanthan exhibited a gel behavior of high value of xanthan fraction. Imeson (1992) said that the galactomannan are composed of mannose chains with galactose side units. The mannose to galactose ratio is an important parameter for the interaction with xanthan gum. Therefore, guar gum, which has a mannose to galactose ratio of around 2: 1, exhibits weak synergism, whereas LBG, with a ratio of about 4:1, reacts more strongly with xanthan gum.

6.5.2 Oscillation test

The measurement of oscillation test was used for investigating the viscoelastic properties of synergistic between guar gum with xanthan gum and LBG with xanthan gum. Oscillation test was measured by using the frequency method from 0.1 to 10 Hz. Results showed that both interaction between guar gum with xanthan gum, and LBG with xanthan gum showed that G' (storage modulus) was higher than G'' (loss modulus). As can be seen in figure 6.20 that G' of mixing gum between guar gum and xanthan gum solution increased compared to a pure gum solution. Therefore, guar fraction enhanced the elastic properties of gum. The highest of G' was at guar gum of 25 %. Thus, the strongest synergistic relation was at that ratio.

As seen in figure 6.21, combination LBG and xanthan gum showed that the synergism was able to improve the storage modulus the same as combination between guar and xanthan gum. It can be seen that G' of mixing gums solution was significantly higher than pure gum solution. Furthermore, the value of G' of mixing gum solution was totally high: up to 200 Pa of G' . It can be described that their combination performed particle gel behavior and exhibited the elastic behavior. The best ratio of LBG and xanthan for setting gel was 50: 50, because G' of it was highest at 215.12 Pa. In the comparison both combination, the LBG combination showed strongly elastic behavior than guar gum combination.

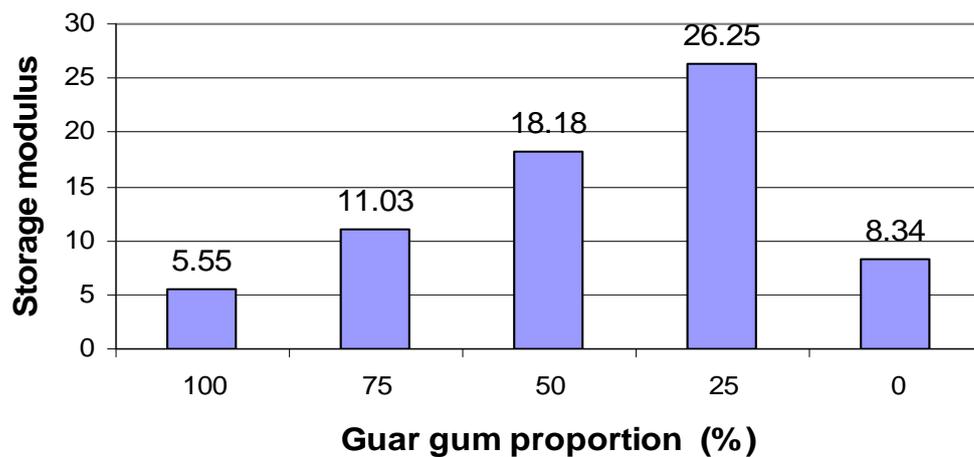


Figure 6.20 Effect of guar gum proportion on storage modulus at frequency of 0.1 Hz

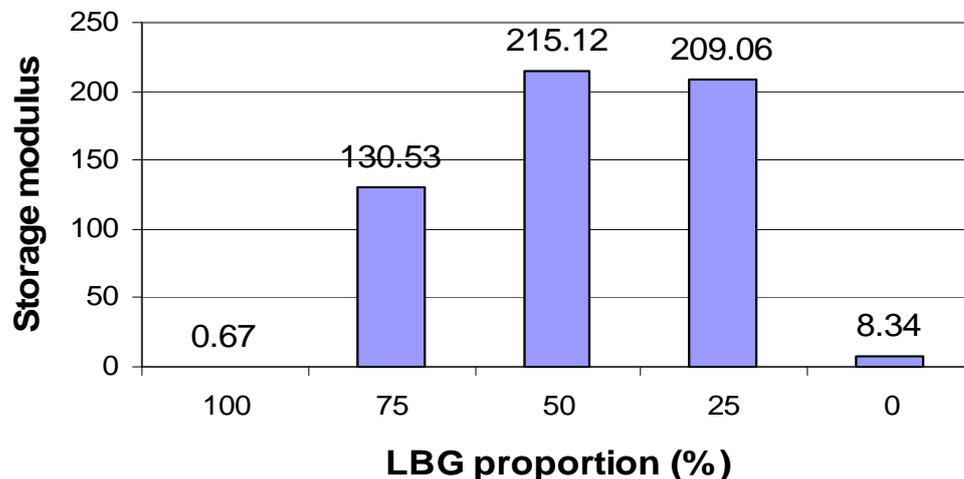


Figure 6.21 Effect of locust bean gum proportion on storage modulus at frequency of 0.1 Hz

Mannion *et. al.* (1992) investigated the interaction between locust bean gum and xanthan gum on rheological properties at room temperature. The results showed the same trend as our: G' was higher than G'' at all range of frequency. The synergism was able to improve the storage modulus. The highest G' was ratio of 50: 50. It confirmed our resulted the mixed gum between LBG and xanthan exhibited the elastic-like behavior

Chapter 7

Material science examination for pineapple puree with stabilizers

Pineapple puree is one important raw material for making the jam, baby food and fruit filling in bakery product, such as donut. However, pineapple puree has a problem with stability after blending process and during storage time. The objective of this study was the application of selected hydrocolloid in order to retain and increase the stability of pineapple puree. The hydrocolloids used in this study, were pectin, guar, locust bean and xanthan gum. Stability was analyzed using the rheological methods, such as shear rate examination and oscillation test.

7.1 Selecting the stabilizers for pineapple puree

The different hydrocolloid was applied in pineapple puree in order to stabilize its structure. The hydrocolloid was used to investigate the impact on stabilizing the pineapple puree structure, with pectin, locust bean gum, guar gum, alginate, carragenan and xanthan gum. All of stabilizers were added in pineapple puree at 1 % of concentration. The method of preparation was depended on requirement of each gum: for example, locus bean gum required dissolving at high temperature; and pectin required the sugar to assist its dispersion ability. However, in the case of pectin, as little sugar as possible was added in order to control the expression of sugar properties. The aim of this study was to select those stabilizers with the potential for use in stabilizing the structure of pineapple puree. In addition, the effect of concentration of gum and temperature on selected stabilizers in pineapple puree was studied in next examination.

Table 7.1 show rheological parameters of pineapple with different stability at concentration of 2 %. This table will showed both models, such as Herschel Bulkley and Ostwald-de Waele models. The control sample use pineapple puree without stabilizer.

Table 7.1 Rheological parameter for pineapple puree added different stabilizers (c = 2%)

Type	OW					HB						
	K Pa·s ⁿ	n	r	η_{eff} (50/s) Pa·s	τ_0 Pa	K Pa·s ⁿ	n	r	A_{TH} Pa·s ⁻¹	η_{eff} (50/s) Pa·s		
Pure puree	0.201	0.672	0.996	0.044	-	0.666	0.162	0.690	0.996	222.00	0.046	√
Pectin	32.69	0.430	0.999	2.368	√	-8.638	40.287	0.396	0.999	984.56	2.409	-
Carragenanan	45.53	0.290	0.999	1.731	√	-14.66	60.694	0.239	0.999	238.55	1.678	-
Alginate	87.57	0.335	0.999	4.096	√	-22.79	111.37	0.287	0.999	809.94	3.948	-
CMC	12.55	0.365	0.991	0.674	√	-19.31	42.87	0.239	0.999	44.37	1.096	-
Guar gum	133.46	0.137	0.914	2.508	√	-2,257	2,387	0.010	0.949	714.00	2.425	-
LBG	48.19	0.366	0.977	2.600	√	-83.43	130.90	0.174	0.998	254.84	2.083	-
Xanthan gum	65.23	0.133	0.997	1.204	√	-111.4	177.01	0.055	0.996	76.95	1.166	-

Figure 7.1 and 7.2 show rheological diagrams; shear stress versus shear rate and effective viscosity versus shear rate of pineapple puree containing different stabilizers; pectin, locust bean gum, guar gum, alginate, carragenan and xanthan gum of 2 % concentration at temperature of 20 °C. The control sample use pineapple puree without stabilizer.

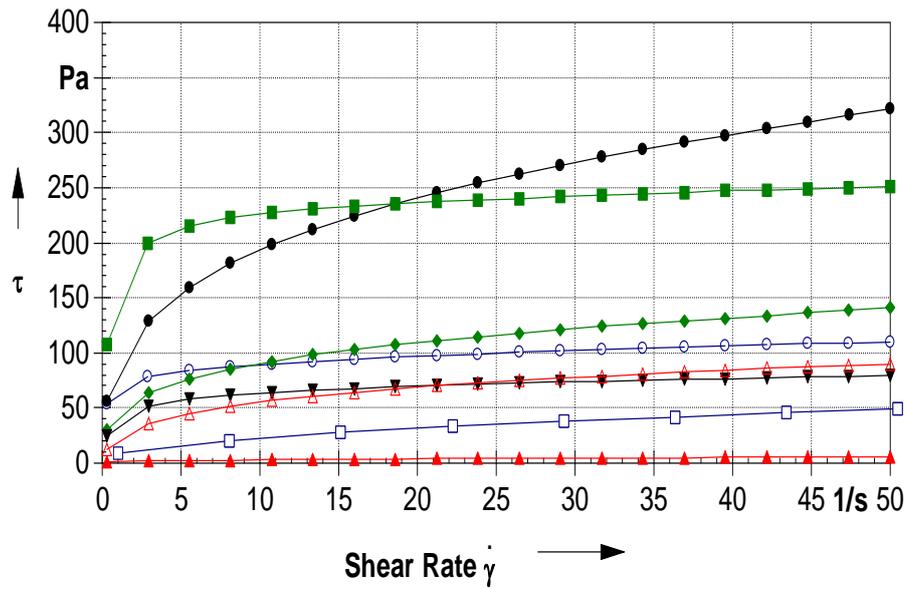


Figure 7.1 CSR-Examination between shear stress and shear rate for pineapple puree with different stabilizers; Pure pineapple puree (▲), Xanthan gum (○), Carragenan (◆), Alginat (●), Locust bean gum (■), Guar gum (▼), CMC (Δ) and pectin (□)

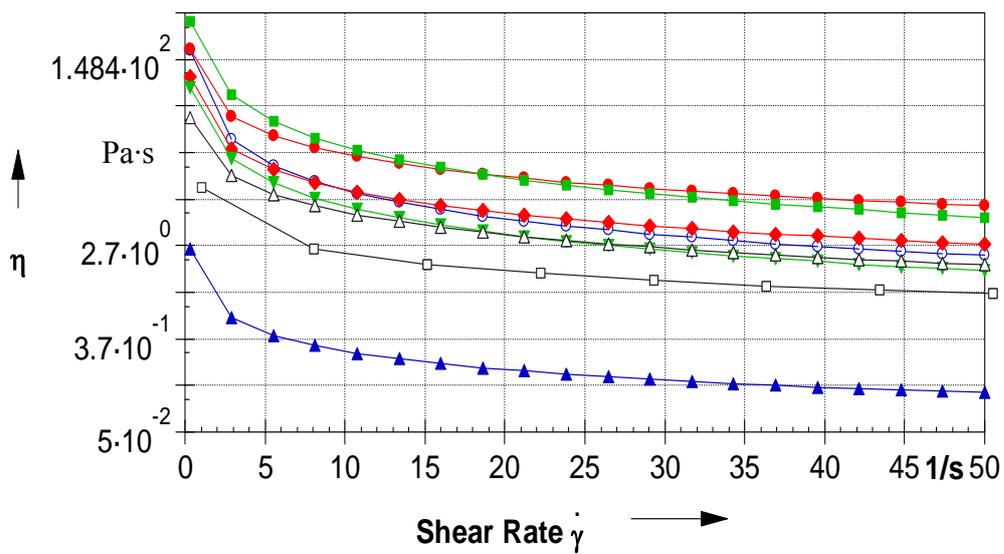


Figure 7.2 CSR-Examination between viscosity and shear rate for pineapple puree with different stabilizers; Pure pineapple puree (▲), Xanthan gum (○), Carragenan (◆), Alginat (●), Locust bean gum (■), Guar gum (▼), CMC (Δ) and pectin (□)

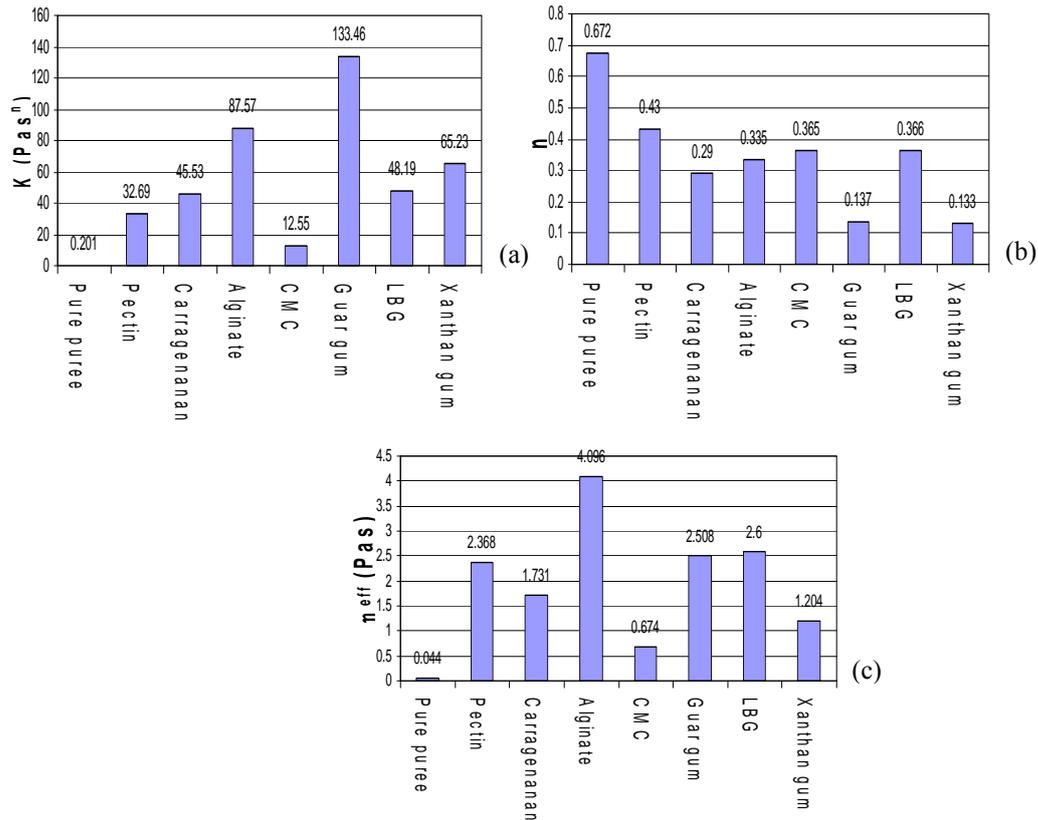


Figure 7.3 Comparison of rheological parameters for pineapple puree with different stabilizers; Consistency factor (a), Flow index (b) and App. viscosity (c)

Results (Table 7.1, Figure 7.1) showed that the flow curves and parameters of pineapple puree added stabilizers matched closely with Ostwald-de Waele model, because the yield point on Herschel-Bulkley model performed the negative value. However, the pineapple puree without stabilizer showed the positive value on yield point value. Pineapple puree changed flow behavior from fluid to semisolid behavior. Thus, only pineapple puree without stabilizer was used in the Herschel-Bulkley model to fit the rheological parameters. Pelegrine *et al.* (2002) studied the rheological behavior of pineapple pulp and mango pulp. The rheological behavior of pineapple pulp was used in the Ostwald-de Waele model. The pineapple pulp performed the structure fluid behavior.

The parameter for each stabilizer was compared base on Ostwald-de Waele model. The highest value of consistency factor (K) was pineapple puree with added guar gum of about 133.46 Pa·sⁿ. On the other hand, the lowest value was pineapple puree without gum. Therefore, the stabilizer was able to improve the consistency factor. Flow index was decreased after added stabilizers. Thus, the structure of pineapple puree was stronger and had more stability compare with pure pineapple puree. In the Comparison between stabilizers, the flow index was for pineapple puree containing guar and xanthan gum lowest. (about 0.137 and 0.133 respectively). Adding LBG and CMC performed middle range of flow index value. Both can be considered to have good potential as stabilizers for pineapple puree. High-DE pectin was the poor stabilizer for pineapple puree. All of stabilizers were able to improve the viscosity of pineapple puree significantly. This was an evident from the increase in viscosity of pineapple puree with added stabilizers. The highest viscosity was in

the pineapple puree with added alginate. Lowest viscosity was found in pineapple puree with CMC added. Therefore, the stabilizer was able to improve the rheological properties of pineapple puree. The sensory test of pineapple puree with each gums showed no difference, because the pineapple puree already had the strong odor and taste of pineapple. Thus the taste of gum was not detected in pineapple puree products.

Grizotto and et al (2006) investigated the restructuring on concentrated pineapple pulp. They used the alginate, low methoxy pectin and glycerol to restructure the pineapple pulp. The restructure rate was measured by firmness. Results showed that the alginate was most effective, increasing firmness values compare with normal concentration pineapple pulp. This result showed the same as our result that alginate could improve the structure of pineapple puree.

To conclusion, the gums with the best potential as stabilizers for pineapple puree are guar gum and xanthan gum. This was because both showed the low flow index value. The locust bean gum was also chosen to represent the middle range of flow index value. Basically pineapple contains some pectin. Pectin was chosen to study the effect of extra pectin added in pineapple puree.

7.2 Examination of material science for pineapple puree with pectin

Although, pineapple puree contains some pectin (0.06 – 0.16 %) (Salunkhe, 1995), but the structure was not fully stable. The evident showed that the phase separation during storage or after blending was occurred. In order to increase among of pectin, pectin was added in pineapple puree and studied some factor. The aim of this study was to investigate the effect of pectin on rheological properties of pineapple puree. Factor of pectin investigated in pineapple puree, included type of pectin, concentration of pectin, Ca-ion interaction and effect of sugar content.

7.2.1 Effect of type and DE of pectin

Pectin was divided into two group base on source which were apple and citrus pectin. Moreover, Pectin was still classified by using level of DE. (Table 7.2) The objective of this study was to investigate the both types and DE effect on pineapple puree structure. The stability properties were invstigated using the shear rate examination. The curve and parameters were fitted by using Herschel-Bulkley and Ostwald-de Waele model.

Table 7.2 Information of pectin in pineapple puree experiment (See. 4.2)

<i>Type of pectin</i>	<i>Source</i>	<i>DE</i>	<i>Code</i>
High DE	Apple	> 70	AU202
Medium DE	Apple	≈ 50	AU607
Low DE	Apple	< 10	AU910
Amidate	Apple	≈ 50	AU L063/05
High DE	Citrus	> 70	CU201
Medium DE	Citrus	≈ 50	CU701
Low DE	Citrus	< 10	CU902
Amidate	Citrus	≈ 50	CU L063/05

Figure 7.4 and 7.5 show rheological diagrams; shear stress versus shear rate and effective viscosity versus shear rate of pineapple puree containing different type of pectin, which classified by level of DE and source of pectin, such as apple and citrus.

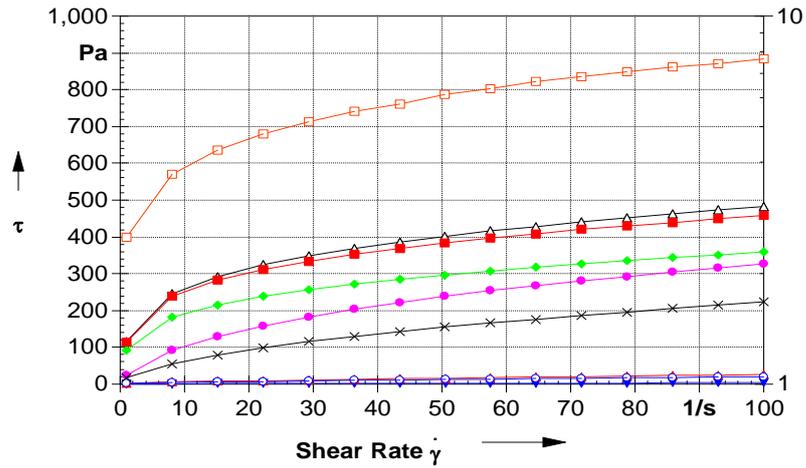


Figure 7.4 CSR-Examination between shear stress and shear rate for pineapple puree added different types of pectin; pure puree (\blacktriangledown), CU902 (\blacktriangle), CU701 (\blacklozenge), CU L063/05 (Δ), CU201 (\bullet), AU910 (\circ), AU607 (\blacksquare), AU L063/05 (\square) and AU202 (X)

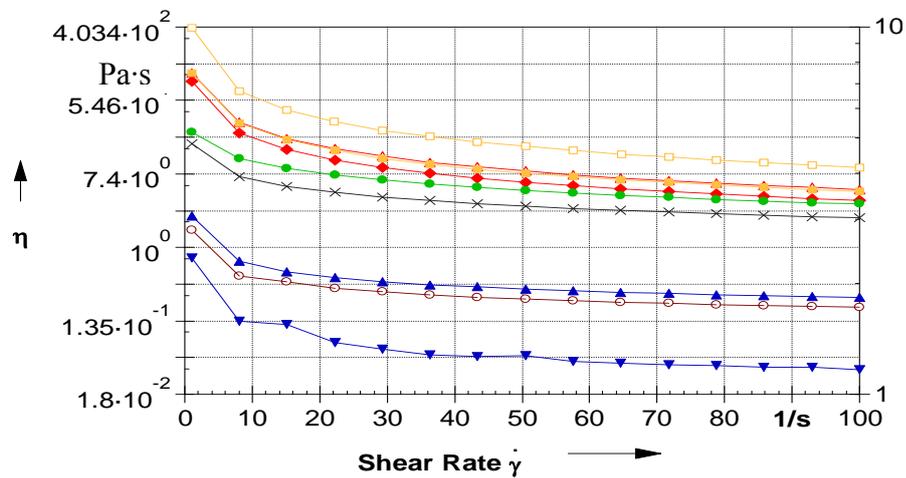


Figure 7.5 CSR-Examination between viscosity and shear rate for pineapple puree added different types of pectin; pure puree (\blacktriangledown), CU902 (\blacktriangle), CU701 (\blacklozenge), CU L063/05 (Δ), CU201 (\bullet), AU910 (\circ), AU607 (\blacksquare), AU L063/05 (\square) and AU202 (X)

Table 7.3 Rheological parameters for pineapple puree added different type of pectin (C = 2%)

Type of pectin	OW					HB						
	K Pa·s ⁿ	n	r	η_{eff} (50/s) Pa·s	τ_0 Pa	K Pa·s ⁿ	n	r	A_{TH} Pa·s ⁻¹	η_{eff} 50/s Pa·s		
Pure puree	0.20	0.672	0.996	0.044	-	0.66	0.162	0.690	0.996	222	0.046	√
AU 910	1.159	0.556	0.965	0.150	-	1.15	0.709	0.725	0.972	1037	0.211	√
AU 607	141.37	0.257	0.993	4.617	√	-75.65	207.59	0.206	0.993	30311	4.604	-
AU 202	18.36	0.548	0.993	2.291	√	-2.98	20.65	0.524	0.993	11494	2.276	-
AU L063/05	446.56	0.136	0.993	8.354	-	151.56	294.20	0.183	0.923	71487	8,349	√
CU 902	2.09	0.551	0.953	0.264	-	1.55	0.980	0.708	0.986	1360	0.271	√
CU 701	114.07	0.250	0.953	3.607	√	-7.51	116.11	0.257	0.953	23521	3.717	-
CU 201	29.96	0.526	0.992	3.377	√	-22.58	48.24	0.432	0.994	16977	3.301	-
CU L063/05	146.95	0.264	0.979	4.956	√	-74.01	204.10	0.217	0.979	31175	4.804	-

Results showed that curves (Figures 7.4 and 7.5) and parameters (Figure 7.3) of pineapple puree without stabilizers was matched with Herschel-Bulkley model closely, because the yield point (τ_0) exhibited positive value. Moreover, pineapple puree to which was added low-DE pectin was also matched with Herschel-Bulkley model, but the yield point was increased compare with pure pineapple puree from 0.666 to 1.15 Pa·sⁿ. Both types of pectin showed the same trend: increase of yield point on low-DE level. In the case of pineapple puree with added higher level of DE, rheological parameters were matched Ostwald-de Waele model, because the yield point performed negative value. Flow behavior of pineapple puree was changed from fluid-like properties to semi-solid properties, when level of DE was higher than 10. It was evident that yield point showed the negative value after added the medium DE.

In the comparison between apple and citrus pectin base on Ostwald-de Waele model, the viscosity of apple pectin was lower than that of citrus pectin at low and high level of DE. However, viscosity of apple pectin was lower than that of citrus pectin at medium level of DE. In the case of amide pectin, the viscosity of apple pectin showed the two times higher than that of citrus pectin. In normal pectin, flow index of citrus pectin was higher than that of apple pectin. Thus, citrus pectin produced the stronger structure than of apple pectin. However, amide pectin showed the opposite way on other pectins. Amide pectin of apple performed lower flow index than of citrus pectin. There was no different of K value, except the amide pectin which was significantly higher than citrus pectin.

The most properties of pectin were depended on the level of DE. As shown, amide pectin was the lowest flow index value on both models. If only normal pectin types are considered, medium-DE pectin showed the lowest flow index value. Thus is because the low level of DE pectin needed the Ca-ion to build the structure and enhance the viscosity. Basically, pineapple contains some Ca-ion, but it is not enough to set the structure between Ca-ion and low-DE pectin. The consistency factor was increased significantly when pectin was added to pineapple puree. The amide pectin showed the highest value of consistency factor and viscosity. It also performed the low flow index value. The good performance of amide pectin in pineapple puree was because amide pectin has all of three factors that hydrogen bonding, hydrophobic interaction and Ca-ion interaction. In contrast, high DE pectin has only water soluble. The low DE pectin was Ca-ion interaction and water soluble.

To conclusion, the amide pectin showed the good stability (low flow index), but the yield point was very high. The yield point showed the strength of structure, such as its high yield point which caused this greater strength. (Canet, 2005) Therefore, the amide pectin had a significantly strong strength and its structure was lost rapidly with shear rate. It can be shown that the amide pectin performed the gel formation in pineapple puree. In the case of low-DE pectin, it can be conclude that it was not suitable to add to pineapple puree, because of low viscosity and low stability (High n value). The medium range of DE showed the good stability, the viscosity was too effective in pineapple puree compare with high-DE pectin. (High viscosity) However, the pineapple puree product did not require the same high viscosity properties as jam product. Therefore, pectin was chosen to continue investigate the effect, that high level of DE pectin.

7.2.2 Effect of concentration of pectin on pineapple puree

High-DE pectin was added in pineapple puree as the extra volume, because pineapple puree already contained some pectin. The aim of this study was to determine the effect of pectin when added to pineapple puree. Pectin used in this study was represented by citrus pectin with high DE value. 10 % concentration of sugar was added. The pectin varied from

1, 2, 2.5 and 3 % of concentration. Rheological properties were measured by using shear rate examination and oscillatory test.

7.2.2.1 Shear rate examination

The shear rate examination was measured by using shear rate $\dot{\gamma}$ up to 50 1/s. A method of measurement was used the five phase method. However, the phase used for calculating parameters was the fifth phases. Figure 7.1 and 7.2 show rheological diagrams; shear stress versus shear rate and effective viscosity versus shear rate of pineapple puree containing pectin at different concentration; 1, 2, 2.5 and 3 %. Table 7.6 show rheological diagrams between shear stress versus shear rate and effective viscosity versus shear rate on pineapple puree containing pectin at different concentration.

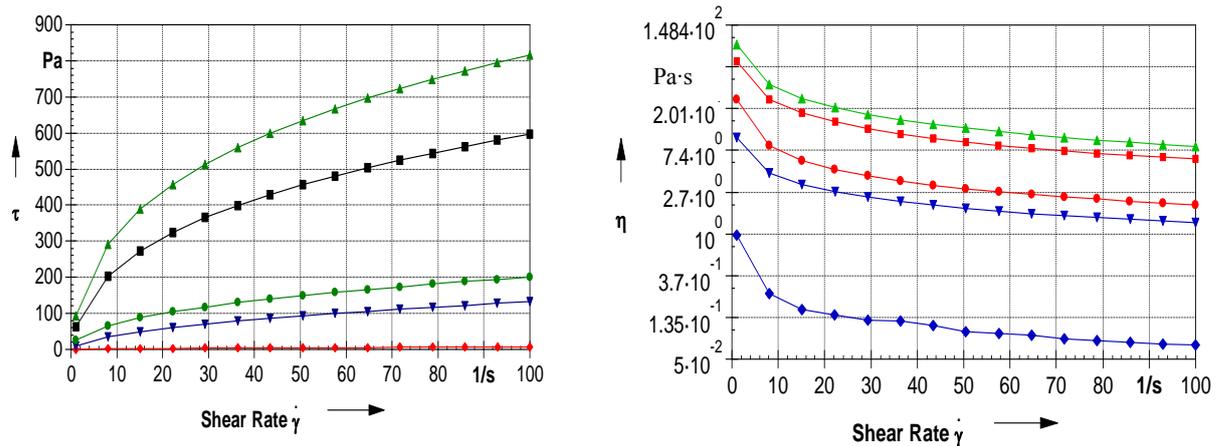


Figure 7.6 CSR-Examinations for pineapple puree with different concentration of pectin; pure puree (\diamond), 1 % (∇), 2 % (\bullet), 2.5 % (\blacksquare) and 3 % (\blacktriangle)

Table 7.4 show the rheological parameters of Herschel Bulkley and Ostwald-de Waele models on pineapple puree containing pectin at different concentration; 1, 2, 2.5 and 3 %. This table show validation of model in each level of concentration.

Table 7.4 Rheological parameters for effect of concentration pectin in pineapple puree

c %	OW				HB							
	K Pa·s ⁿ	n	r	η_{eff} (50/s) Pa·s	τ_0 Pa	K Pa·s ⁿ	n	r	A_{TH} Pa/s	η_{eff} (50/s) Pa·s		
0	0.201	0.672	0.996	0.044	-	0.66	0.162	0.690	0.996	222	0.046	√
1	11.09	0.543	0.996	1.352	√	-2.82	13.33	0.506	0.997	6,198	1.342	-
2	29.96	0.526	0.992	3.377	√	-22.5	48.24	0.432	0.994	16,977	3.301	-
2.5	81.42	0.443	0.985	6.262	√	-50.18	121.79	0.369	0.988	33,037	6.160	-
3	124.11	0.420	0.982	8.586	√	-86.50	194.78	0.341	0.983	45,657	8.501	-

The model used for fitting the curve (Figure 7.6) and parameters was Ostwald-de Waele model. The reason was that the yield point of Herschel-Bulkley model (Table 7.4) showed the negative result on pineapple puree with added pectin. However, there was only pineapple puree without pectin exhibit the positive yield point. According to table 7.4, thixotropic area was increased with concentration. Thus, pineapple puree with high concentration of pectin used higher energy of flow. The flow index was decreased with concentration. Thus, the structure was more stable when pineapple puree had a high concentration of pectin added. The viscosity was increased with concentration logically.

Figure 7.7 show predicted diagrams of rheological parameters for pineapple containing pectin at different concentration. This diagrams validated on concentration of 1 to 3 % and shear rate of 0.1 to 50.

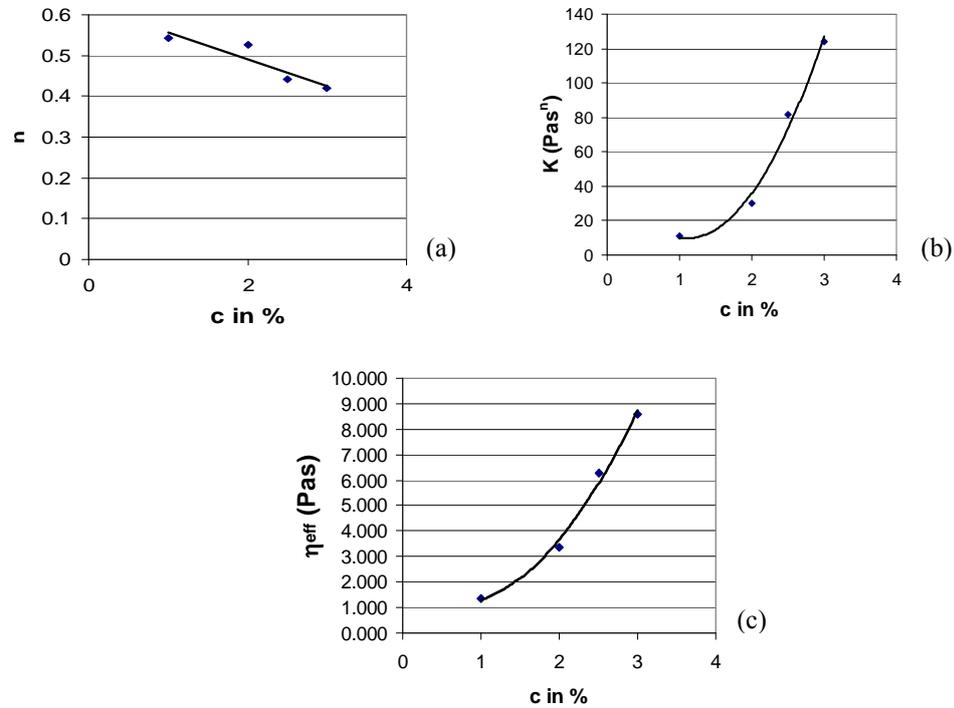


Figure 7.7 Trend diagram of rheological parameters for effect of concentration;
Consistency factor (a), Flow index (b) and Viscosity (c)

The trend of concentration effect was showed in figure 7.7 that the consistency factor (K) increased with concentration. The trend diagram fitted with polynomial equation (Eq. 7.1). The flow index (n) decreased with concentration. The trend diagram fitted with linear equation (Eq. 7.2) Viscosity parameter (η_{eff}) was increased with concentration. The prediction trend was fitted with polynomial equation. (Eq. 7.3)

$$K(c) = 32.624 \cdot c_{pec}^2 - 71.978 \cdot c_{pec} + 49.441 \quad \text{in Pa} \cdot \text{s}^n \quad r = 0.987 \quad (\text{Eq. 7.1})$$

$$n(c) = -0.0654 \cdot c_{pec} + 0.6219 \quad r = 0.968 \quad (\text{Eq. 7.2})$$

$$\eta_{eff}(c) = 1.3453 \cdot c_{pec}^2 - 1.6651 \cdot c_{pec} + 1.6223 \quad \text{in Pa} \cdot \text{s} \quad r = 0.995 \quad (\text{Eq. 7.3})$$

*Validity: $0.1 \leq \dot{\gamma} \leq 50/\text{s}$ and $1 \leq c_{pec} \leq 3 \%$

7.2.2.2 Oscillation test

To study the viscoelasticity of pineapple puree with different concentration of pectin, the measurement was used the frequency sweep range from 0.01 to 10 Hz. The data presented in Storage modulus and $\tan \delta$ parameter. Table 7.8 show Oscillation diagrams at frequency sweep methods for pineapple puree containing pectin at different concentrations.

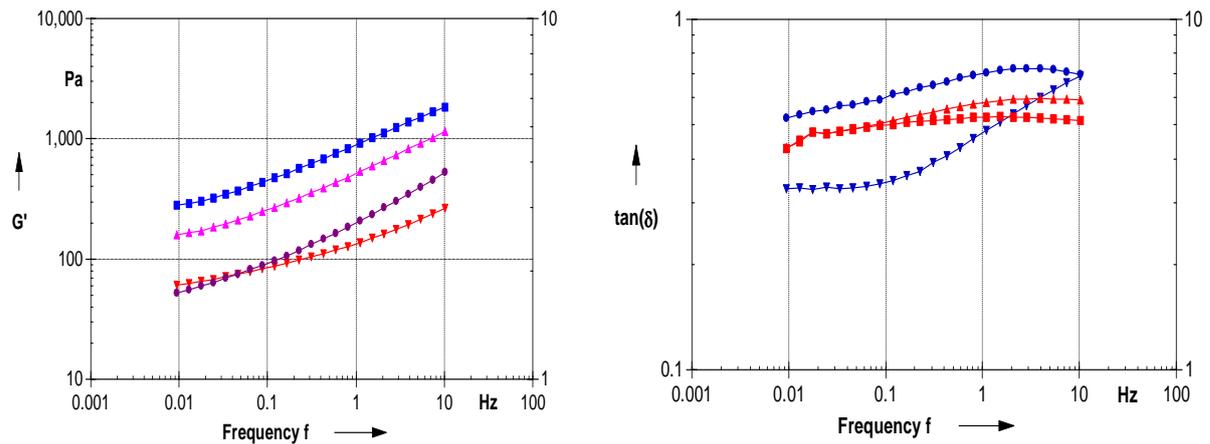


Figure 7.8 Frequency sweep diagrams for puree with different concentration; 1% (\blacktriangledown), 2% (\bullet), 2.5% (\blacktriangle) and 3% (\blacksquare)

The result showed that G' (Storage modulus) was higher than G'' (Loss modulus) of all sample at all range of frequency. Diagrams (Figure 7.8) performed a slope for G' and G'' . Thus, the pineapple puree with pectin had a semisolid behavior with particle dispersion system. G' value was increased with frequency and concentration. The highest G' was at 3% of concentration. However, the slope of sample of 2% of concentration was lower than 1% pectin sample. The $\tan \delta$ value exhibited a non-identifiable trend with sample concentration, where as the $\tan \delta$ of 2% of concentration was highest compare when compared at frequency of 1 Hz.

7.2.3 Effect of sugar content

Pineapple puree has sugar as one of its ingredients: in particularly, pineapple puree with added pectin, because sugar assisted the dispersion property of pectin. The aim of this study was to analyze the role of sugar in pineapple puree. In this study, six level of sugar content were added to the pineapple puree, at 10, 20, 30, 40, 50 and 60% of sugar concentration. The pectin was used in pineapple puree in this study contained high-DE citrus pectin (CU202). The structure of pineapple puree was analyzed by using the rheological properties (Shear rate examination and oscillation test)

7.2.3.1 Shear rate examination

To study the effect of sugar content on the structure in pineapple puree with pectin, the macro structure of the puree was determined by using the control shear rate examination with five phase of measurement at $0.1 \leq \dot{\gamma} \leq 50/s$. Parameters were calculated in the fifth phase of diagrams. Figure 7.9 show rheological diagrams between shear stress versus shear rate and effective viscosity versus shear rate on pineapple containing pectin concentration of 2% and different percent of sugar; 10, 20, 30, 40, 50 and 60%.

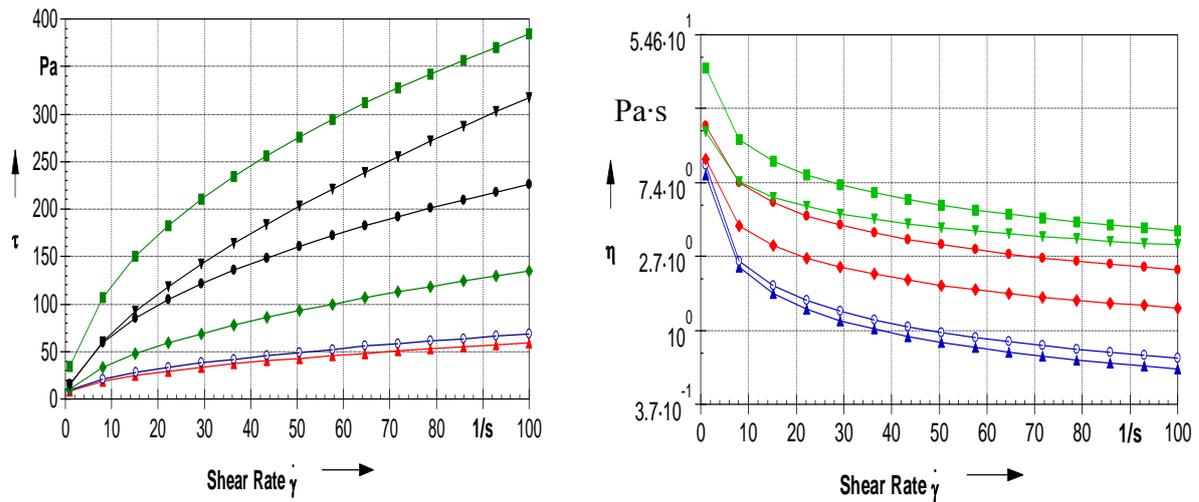


Figure 7.9 CSR-Examination of pineapple puree with pectin and different sugar concentration; 10 % (\blacktriangle), 20 % (\circ), 30 % (\blacklozenge), 40 % (\bullet), 50 % (\blacksquare) and 60 % (\blacktriangledown)

Table 7.5 show rheological parameters of Herschel Bulkley and Ostwald-de Waele model for pineapple containing pectin concentration of 2 % and different percent of sugar; 10, 20, 30, 40, 50 and 60 %.

Table 7.5 Rheological parameters for effect of sugar content in pineapple puree

c %	OW					HB						
	K Pa·s ⁿ	n	r	η_{eff} (50/s) Pa·s	τ_0 Pa	K Pa·s ⁿ	n	r	A_{TH} Pa/s	η_{eff} (50/s) Pa·s		
0	0.201	0.672	0.996	0.044	-	0.66	0.162	0.690	0.996	222	0.046	✓
10	32.70	0.437	0.993	2.446	✓	-8.63	40.28	0.396	0.996	5,734	2.409	-
20	34.64	0.443	0.997	2.663	✓	-16.44	52.08	0.357	0.999	8,564	2.531	-
30	37.33	0.479	0.996	3.388	✓	-24.37	58.77	0.374	0.999	12,947	3.046	-
40	59.19	0.481	0.993	5.423	✓	-56.63	109.85	0.402	0.999	18,004	6.428	-
50	88.39	0.493	0.995	8.558	✓	-41.21	128.30	0.401	0.997	22,700	7.720	-
60	33.75	0.566	0.995	4.574	✓	-8.78	39.94	0.532	0.960	20,006	4.540	-

Results showed that the parameters matched the Ostwald-de Waele model, because the yield point (τ_0) in Herschel-Bulkley model performed negative value. (Table 7.5) Flow index of pineapple puree was decreased after adding pectin and sugar compared with pineapple puree without pectin. However, the flow index was increased when a greater concentration of sugar was added to the puree. It can be described that the sugar was able to improve the structure stability of pineapple puree very well at low sugar concentration, but the stability improvement was reduced as seen by the increase in the flow index. It can be explained the sugar particles interfered blinding between pectin and the pineapple puree. The consistency factor (K) results showed that the K value increased with sugar concentration until the 50 % of sugar concentration. The result of viscosity showed the same tendency: the viscosity was increased with sugar concentration until 50 %.

All of these results can be explained by the sugar having ability to increased stability compare with pure puree. At high concentration of sugar, the sugar particle was interfered the blinding between pectin and puree. This was due to sugar used the free water instead of pectin. Thus pectin was not able to show fully water soluble ability. It was the evident that the viscosity decreased rapidly at 60 % of concentration from 8.558 to 4.574 Pa·s. The

prediction diagrams of rheological parameters for pineapple pure containing different concentration of sugar report on figure 7.10

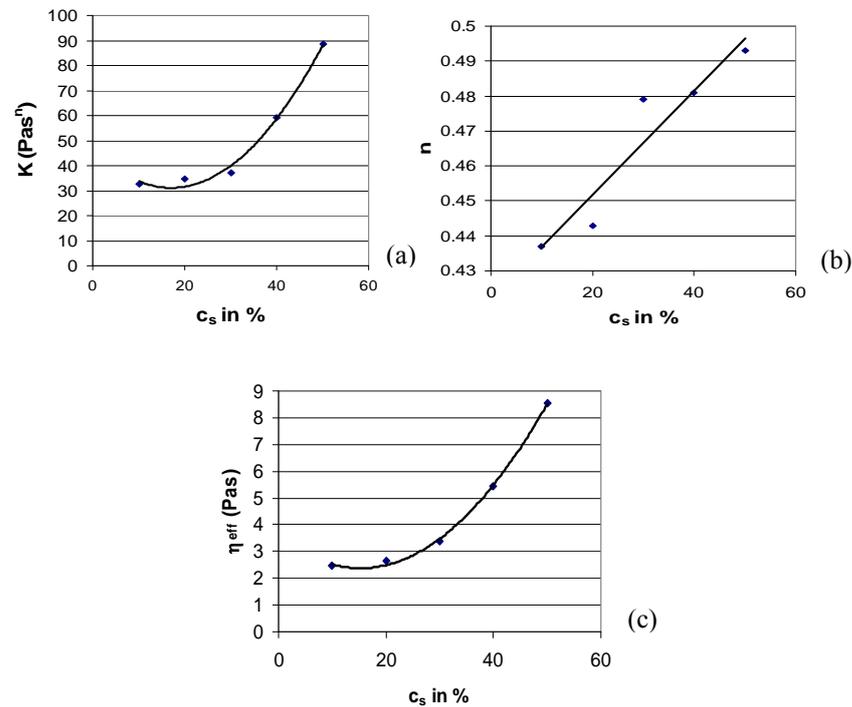


Figure 7.10 Trend diagram of rheological parameters for effect of sugar concentration; Consistency factor (a), Flow index (b) and effective viscosity (c)

The trend of sugar concentration effect was calculated by using a concentration between 10 to 50 %. (Figure 7.10) The consistency factor (K) produced an increasing trend. The trend line fitted with polynomial equation (Eq. 7.4) the trend line of flow index (n) also increased with sugar concentration. The trend line fitted with Polynomials equation. (Eq. 7.5) The viscosity trend also showed an increase. The trend line fitted with Polynomial equation. (Eq. 7.6)

$$K(c) = 0.0526 c_s^2 - 1.7986 c_s + 46.508 \quad \text{in Pa} \cdot \text{s}^n \quad r = 0.998 \quad (\text{Eq. 7.4})$$

$$n(c) = 0.0015 \cdot c_s + 0.4216 \quad r = 0.950 \quad (\text{Eq. 7.5})$$

$$\eta_{\text{eff}}(c) = 0.0051 \cdot c_s^2 - 0.1564 \cdot c_s + 3.5734 \quad \text{in Pa} \cdot \text{s} \quad r = 0.999 \quad (\text{Eq. 7.6})$$

*Validity: $0.1 \leq \dot{\gamma} \leq 50$ 1/s and $10 \leq c_s \leq 50$ %

7.2.3.2. Oscillation test

The micro structure of pineapple puree with pectin and different sugar concentration was determined by using Oscillation test with the Frequency sweep method from 0.01 to 10 Hz. Result (Figure 7.11) showed that storage modulus (G') was higher than loss modulus (G'') at all range of frequency. Thus, the crossover between both parameters did not occur. It can be described that the pineapple puree with sugar and pectin showed the semi-solid

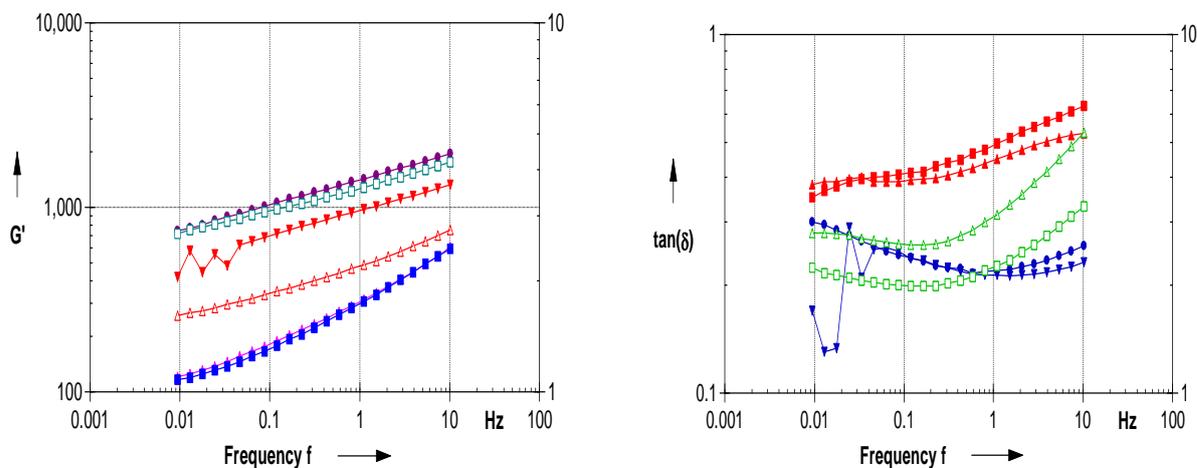


Figure 7.11 Oscillation diagram of puree with pectin and different level of sugar contents; 10 % (\blacktriangledown), 20 % (\bullet), 30 % (\blacktriangle), 40 % (\blacksquare), 50 % (\square) and 60 % (Δ)

7.3 Examination of material science for pineapple puree with locust bean gum

Locust bean gum (LBG) was the one of widely use as stabilizer, for example with its application in infant food (Miyazawa, 2006) or application in the rice cake product (Elif, 2006). The aim of this study was to use the locust bean gum in pineapple puree in order to enhance the stability and viscosity. The reason was that the structure of pineapple puree was not stable during the storage and after blending. The locust bean gum was used to investigate the effects on pineapple puree, such as the effect of concentration of LBG on pineapple puree or the effect on temperature after adding the LBG to pineapple puree. This study used the rheology method for measuring the pineapple puree properties. (Shear rate examination, Oscillation test)

7.3.1 Effect of concentration of locust bean gum on pineapple puree

To study the effect of concentration on pineapple puree, LBG was added to pineapple puree in different concentration: 0.2, 0.4, 0.6, 0.8, 1, 2, 3 and 4. The rheological properties of the sample were measured by emphasizing the stability of puree structure. The rheological methods used in this study were shear rate examination with five phases of measurement ($0 \leq \dot{\gamma} \leq 50/s$). The model was used for describing parameters and curves were Herschel-Bulkley and Ostwald-de Waele models. The parameters were calculated in the fifth phase of diagrams.

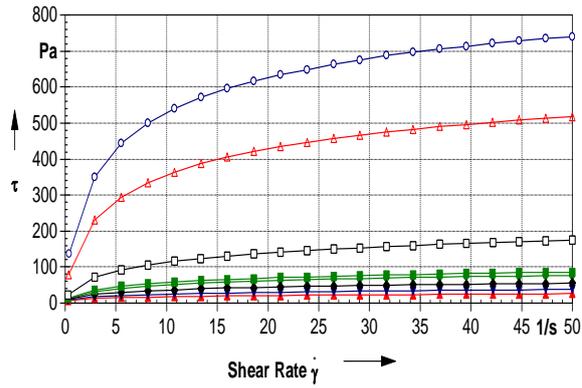


Figure 7.12 CSR-Examination between shear stress and shear rate for pineapple puree with different concentration of LBG; 0.2 % (\blacktriangle), 0.4 % (\blacktriangledown), 0.6 % (\bullet), 0.8 % (\blacklozenge), 1% (\blacksquare), 2 % (\square), 3 % (\triangle) and 4 % (\circ)

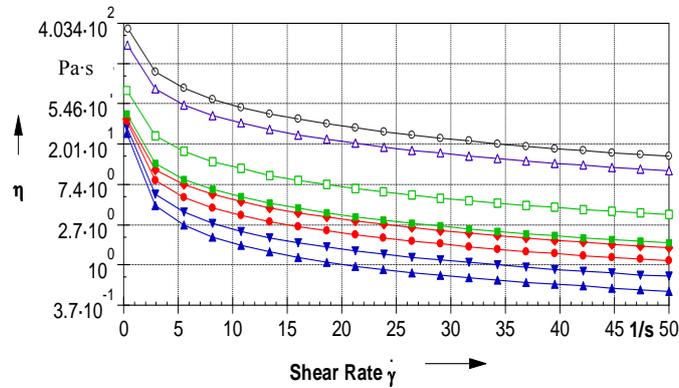


Figure 7.13 CSR-Examination between viscosity and shear rate for pineapple puree with different concentration of LBG; 0.2 % (\blacktriangle), 0.4 % (\blacktriangledown), 0.6 % (\bullet), 0.8 % (\blacklozenge), 1% (\blacksquare), 2 % (\square), 3 % (\triangle) and 4 % (\circ)

Table 7.6 Rheological parameters for effect of LBG concentration on pineapple puree

c %	OW					HB						
	K Pa·s ⁿ	n	r	η_{eff} (50/s) Pa·s	τ_0 Pa	K Pa·s ⁿ	n	r	A_{TH} Pa·s ⁻¹	η_{eff} (50/s) Pa·s		
0	0.201	0.672	0.996	0.044	√	0.66	0.162	0.690	0.996	222	0.046	-
0.2	10.06	0.238	0.998	0.301	√	0.52	7.490	0.292	0.999	28.04	0.313	-
0.4	12.79	0.277	0.999	0.458	√	0.36	12.420	0.283	0.999	59.19	0.461	-
0.6	16.57	0.312	0.993	0.697	√	-9.09	26.01	0.235	0.998	51.81	0.677	-
0.8	20.10	0.362	0.979	1.065	√	-25.94	47.261	0.202	0.997	49.88	0.939	-
1	22.90	0.358	0.979	1.191	√	-37.49	80.937	0.183	0.998	142.9	1.505	-
2	48.19	0.366	0.977	2.600	√	-83.43	130.95	0.174	0.998	254.82	2.084	-
3	144.05	0.350	0.968	7.220	√	-188.5	261.48	0.130	0.909	759.48	2.873	-
4	228.67	0.342	0.966	10.074	√	-1,279	1,518	0.074	0.999	981.68	8.554	-

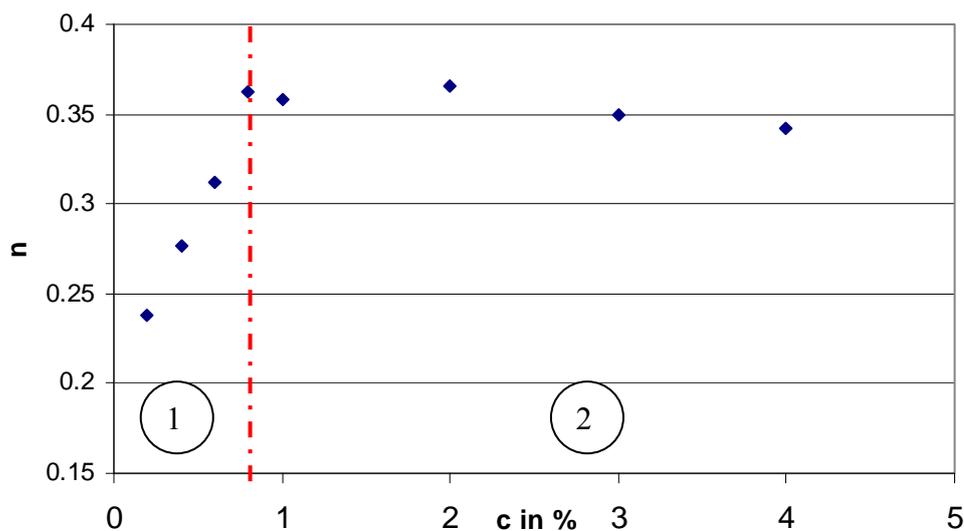


Figure 7.14 Flow index parameter for puree with different concentration of LBG

The result (Table 7.6) showed that the low concentration (0 to 0.4 %) of LBG samples matched closely the Herschel-Bulkley model, because yield point (τ_0) exhibited positive value. The yield point showed a decreased trend with increasing concentration. After 0.6 % of LBG concentration, the yield point showed a negative value, so the model was fitted with parameters, that Ostwald-de Waele model. It can be described that the flow behavior of pineapple puree was changed from fluid behavior to semi-solid behavior when more than 0.4 % of concentration was added. The consistency factor (K) base on Ostwald-de Waele model increased with concentration of LBG. The value of consistency factor increased rapidly at 2 % of concentration.

According to Figure 7.14, the behavior of pineapple puree with locust bean gum was divided into 2 phases by using the flow index parameter. The low concentration of LBG (0 to 0.8 %) significantly showed the increasing trend with concentration. After 0.8 % of concentration, the flow index was steady around 0.35. It can be described that the low range concentration (0.2 to 0.8 %) showed the more effective stability properties than high range of concentration (> 0.8 %). Low concentration was suitable for stabilizing the structure of puree. The effect of concentration on viscosity showed that the viscosity was increased with concentration, logically. The viscosity was increased dramatically at concentration of 3 %. The locust bean gum at low concentration (0.2 %) was especially suitable for stabilizing the structure of pineapple puree. This was because locust bean gum performed the good stability at low concentration and the viscosity was not much changed. Thus, there is no impact on viscosity of pineapple puree product when locust bean gum added. Furthermore, pineapple puree only used little among of LBG. Consequently, pineapple puree produced the good stability of its structure. Therefore, it can reduce stabilizer to adding to pineapple puree.

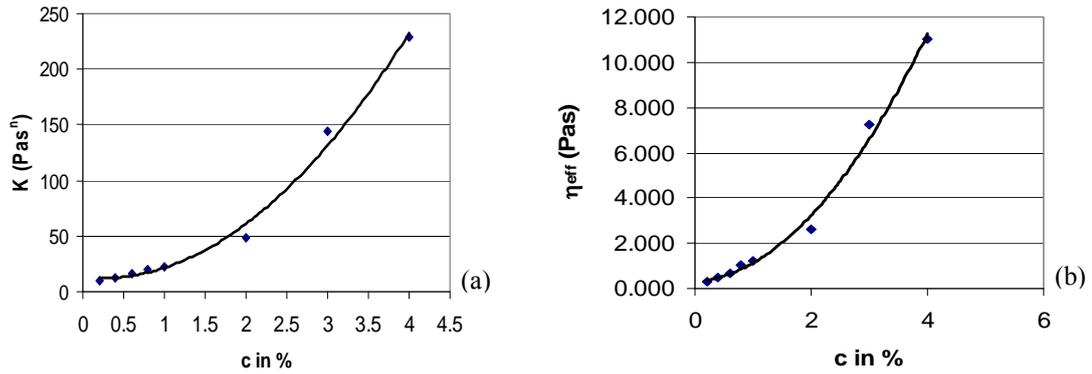


Figure 7.15 Trend diagram of rheological parameters for effect of LBG concentration; Consistency factor (a) and effective viscosity (b)

The trend of flow index (n) for concentration effect was divided into two state of concentration. (Figure 7.15) Thus, the predicted line of flow index at first state of concentration matched the linear equation (Eq 7.7) which showed an increasing trend. In contrast, the trend line of flow index at second state of concentration exhibited steady trend, matched with polynomial equation. (Eq. 7.8) The consistency factor trend (K) exhibited the increasing value with concentration. The trend line matched the polynomial equation. (Eq. 7.9) The viscosity trend (η_{eff}) also showed an increasing trend with concentration. The trend line was matched polynomial equation. (Eq. 7.10)

$$n(c, 1^{\text{st}} \text{ state}) = 0.2035 \cdot c_{\text{lbG}} + 0.1955 \quad r = 0.995 \quad (\text{Eq. 7.7})$$

$$n(c, 2^{\text{nd}} \text{ state}) = -0.0034 c_{\text{lbG}}^2 + 0.0101 \cdot c_{\text{lbG}} + 0.3546 \quad r = 0.920 \quad (\text{Eq. 7.8})$$

$$K(c) = 15.396 c_{\text{lbG}}^2 - 6.5992 c_{\text{lbG}} + 12.771 \quad \text{in Pa} \cdot \text{s}^n \quad r = 0.995 \quad (\text{Eq. 7.9})$$

$$\eta_{\text{eff}}(c) = 0.6339 c_{\text{lbG}}^2 + 0.2008 c_{\text{lbG}} + 0.2987 \quad \text{in Pa} \cdot \text{s} \quad r = 0.995 \quad (\text{Eq. 7.10})$$

*Validity: $0.1 \leq \dot{\gamma} \leq 50$ 1/s and $0.2 \leq c \leq 1$ %

In the case of locust bean gum added to the puree product in order to increase the stability, Sahin and Öydemir (2007) studied the effect of some hydrocolloid on serum of ketchup. The locust bean gum was added to ketchup at 0.5 and 1 % concentrations. The power law model was used for matching parameters. The Flow index value showed the same trend as our results: the flow index increased with concentration. Locust bean gum was found to be more successful more than CMC or tragacanth gum in decreasing the serum separation of ketchup. The concentration of gums play a crucial role in both reducing and slowing down the serum separation of ketchups. Beside the ketchup product, the locust bean gum was also used in fruit filling as one of ingredient. Wei *et al.* (2000) study flow properties of fruit filling, such as apple, blueberry lemon and raspberry puree. Locust bean gum was added in fruit filling at 0.15 and 0.30 % of concentration. Results showed the same as our result: the parameters could be described by Herschel-Bulkley models. The LBG showed the good improvement of viscosity and stability in those puree

7.3.2 Effect of temperature of pineapple puree with locust bean gum

Temperature was the one of effect on pineapple puree product. The temperature of pineapple puree was importance factor of rheological properties, such as stability and viscosity. Normally, semi-solid food properties are depending on the temperature of product. In industries, temperature of puree was seriously concerned. Temperature has an impact to flow of puree in pipe line. The aim of this study was to investigate the effect of temperature on pineapple puree after adding LBG. The rheological measurement of pineapple puree with locust bean gum was measured at 20, 30, 40, 50 and 60 °C. The model was used for matching the parameters were the Herschel-Bulkley and Ostwald-de Weale models. The trend of data was analyzed by using RSM methods.

Table 7.7 Rheological parameters for effect of temperature on pineapple puree with LBG

<i>c</i> %		<i>t</i> ₂₀	<i>t</i> ₆₀	ΔK^* (20-60 °C) Pa·s ⁿ	Δn^* (20-60 °C) -	$\Delta \eta_{eff} (50/s)^*$ (20-60 °C) Pa·s
0.2	HB	τ_0 : 0.520 n : 0.292 K : 7.490 r : 0.999 η_{eff} : 0.313	HB	8.038	(-) 0.139	0.186
			τ_0 : 0.350 n : 0.422 K : 1.651 r : 0.999 η_{eff} : 0.119			
			HB			
			τ_0 : 0.366 n : 0.283 K : 12.42 r : 0.999 η_{eff} : 0.461			
			τ_0 : 0.138 n : 0.506 K : 1.775 r : 0.999 η_{eff} : 0.020			
0.4	HB	τ_0 : 0.366 n : 0.283 K : 12.42 r : 0.999 η_{eff} : 0.461	HB	10.861	(-) 0.208	0.278
			τ_0 : 0.138 n : 0.506 K : 1.775 r : 0.999 η_{eff} : 0.020			
			OW			
			n : 0.312 K : 16.570 r : 0.993 η_{eff} : 0.697			
			n : 0.472 K : 5.190 r : 0.995 η_{eff} : 0.4568			
0.6	OW	τ_0 : 0.366 n : 0.283 K : 12.42 r : 0.999 η_{eff} : 0.461	OW	13.814	(-) 0.208	0.395
			n : 0.312 K : 16.570 r : 0.993 η_{eff} : 0.697			
			OW			
			n : 0.362 K : 20.100 r : 0.979 η_{eff} : 1.065			
			n : 0.468 K : 6.413 r : 0.998 η_{eff} : 0.553			
0.8	OW	τ_0 : 0.366 n : 0.283 K : 12.42 r : 0.999 η_{eff} : 0.461	OW	13.687	(-) 0.106	0.511
			n : 0.312 K : 16.570 r : 0.993 η_{eff} : 0.697			
			OW			
			n : 0.362 K : 20.100 r : 0.979 η_{eff} : 1.065			
			n : 0.468 K : 6.413 r : 0.998 η_{eff} : 0.553			
1	OW	τ_0 : 0.366 n : 0.283 K : 12.42 r : 0.999 η_{eff} : 0.461	OW	12.928	(-) 0.038	0.573
			n : 0.312 K : 16.570 r : 0.993 η_{eff} : 0.697			
			OW			
			n : 0.358 K : 29.900 r : 0.979 η_{eff} : 1.554			
			n : 0.396 K : 9.972 r : 0.998 η_{eff} : 1.215			

* Calculation of parameters difference was base on Ostwald-de Waele model

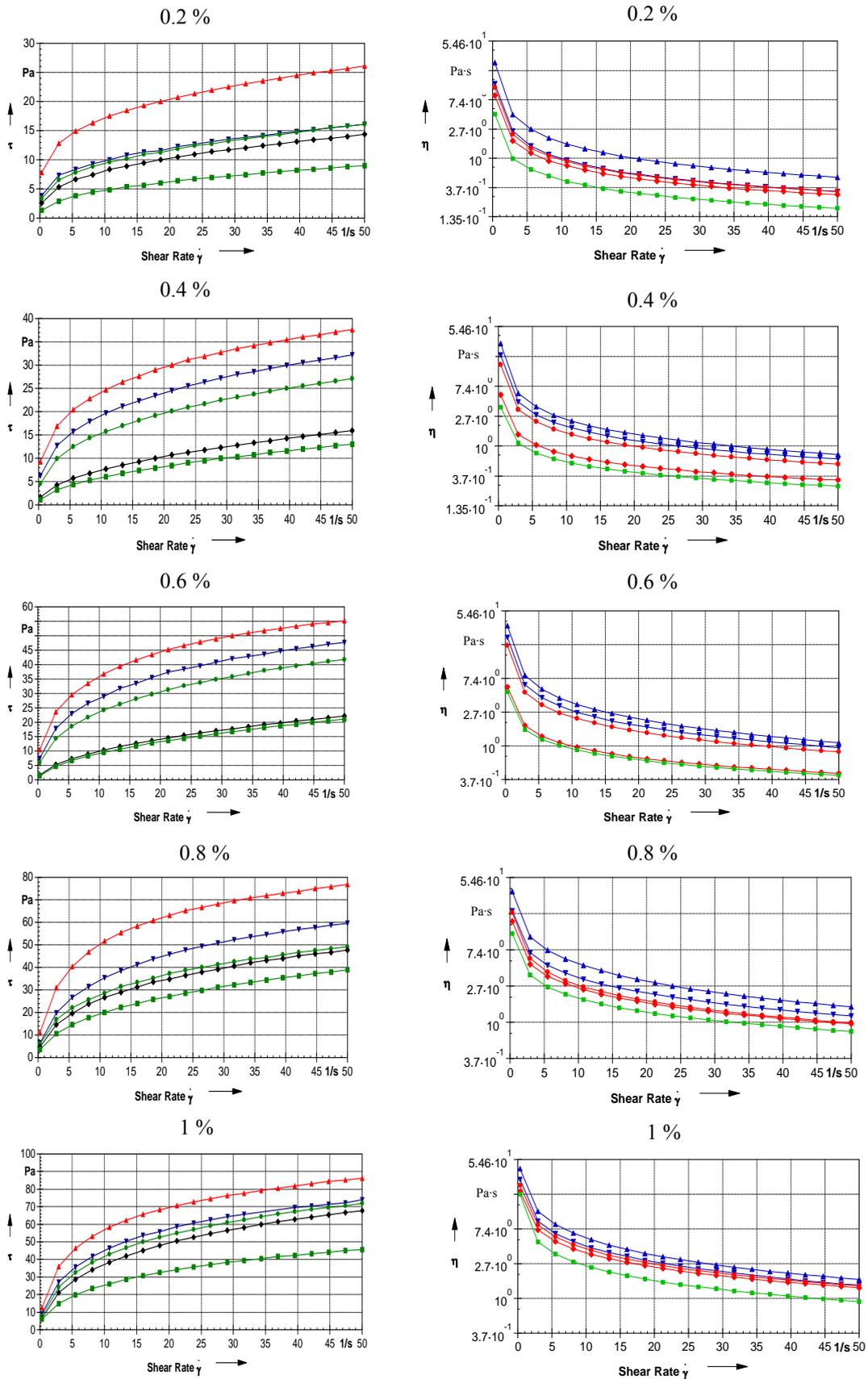


Figure 7.16 CSR-Examination for pineapple puree with different concentration of LBG and temperature; 20 °C (▲), 30 °C (▼), 40 °C (●), 50 °C (◆) and 60 °C (■)

Results (Table 7.7, Figure 7.16) showed that parameters of LBG at concentration of 0.2 and 0.4 % matched the Herschel-Bulkley model at all range of temperature (20 to 60 °C), because the yield point (τ_0) performed a positive value and caused a decreasing trend with temperature. The high concentration of more than 0.6 % was used in the Ostwald-de Waele model for matching parameters at all range of temperature. (20 to 60 °C) It was because the yield point of those ranges of concentration showed negative value. It can be explained that the pineapple puree with low concentration (0.2 and 0.4 %) exhibited the semisolid behavior with yield point.

The difference of consistency factor (ΔK) showed positive value at all range of temperature. Thus, the consistency factor decreased with temperature at all range of concentration. Moreover, ΔK value increased with concentration. Therefore, temperature has influence on K value with high concentration of locust bean gum more than low concentration. The difference of flow index (Δn), flow index produced the negative value at all range of concentration, so the flow index decreased with temperature. It can be explained that the stability of pineapple puree structure was logically reduced with increase in the temperature.

The difference between flow index (Δn) at all range of concentration exhibited an increasing trend with concentration. Thus, temperature affected the stability of pineapple puree with high concentration of locust bean gum more than low concentration. It can be described that the structure of pineapple puree with high concentration has good tolerance with temperature or strong structure system. The difference of viscosity ($\Delta \eta_{\text{eff}}$) showed positive value at all range of concentration, so the viscosity was decreased with increasing temperature. The relationship between concentration and temperature on viscosity showed that the $\Delta \eta_{\text{eff}}$ between 20 to 60 °C was increased with concentration. Thus, the temperature has influence with high concentration of locust bean gum more than low concentration in pineapple puree.

Prediction diagrams for effect of concentration and temperature on pineapple puree with locust bean gum are shown in figure 7.17. Trends of consistency factor (K) increased with concentration and decreasing temperature. The highest value of K value was at 4 % of concentration and temperature of 20 °C. The trend line of it matched with linear equation (Eq. 7.11) Trend of flow index (n) increased with temperature and decreased with an increase in concentration. The lowest value of n was at 4 % of concentration and temperature of 20 °C. The trend line matched the linear equation (Eq. 7.12) Trend of viscosity decreased with temperature and increased with concentration. A highest value of viscosity was at 4 % of concentration and temperature of 20 °C. The trend line matched with linear equation. (Eq. 7.13)

$$K(c, t) = 17.6893 + 39.2367 \cdot c_{\text{lbG}} - 0.8598 \cdot t \quad \text{in Pa} \cdot \text{s}^n \quad r = 0.951 \quad (\text{Eq. 7.11})$$

$$n(c, t) = 0.3114 - 0.0107 \cdot c_{\text{lbG}} + 0.0022 \cdot t \quad r = 0.819 \quad (\text{Eq. 7.12})$$

$$\eta_{\text{eff}}(c, t) = 0.9212 + 1.905 \cdot c_{\text{lbG}} - 0.0392 \cdot t \quad \text{in Pa} \cdot \text{s} \quad r = 0.961 \quad (\text{Eq. 7.13})$$

*Validity: $20 \leq t \leq 60$ °C and $0.2 \leq c_{\text{lbG}} \leq 1$ %

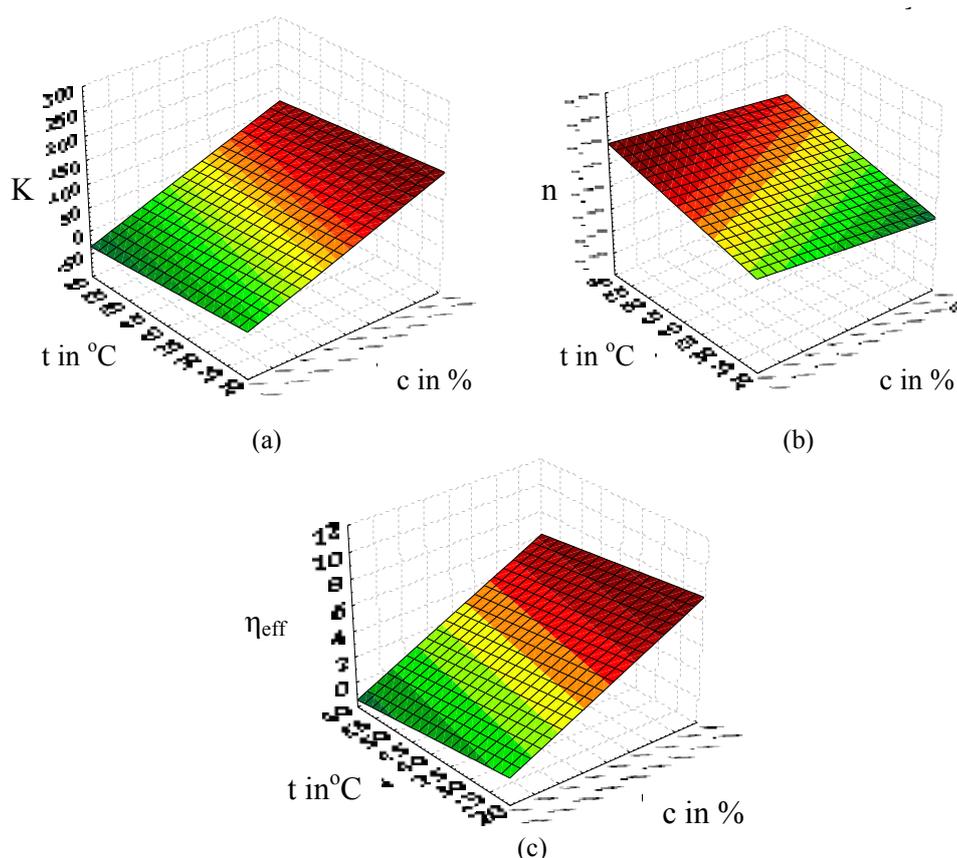


Figure 7.17 RSM diagram of rheological parameters for effect of concentration and temperature on pineapple puree with LBG; consistency factor (a), flow index (b) and viscosity (c)

The E_a or Flow activate energy of pineapple puree with locust bean gum exhibited a non-identifiable trend, whereas the highest of E_a was at concentration of 0.4 % about 20159 kJ/mol. The lowest of E_a was at 1 % of concentration about 10970 kJ/mol.

Table 7.8 Flow activate energy for temperature changing of pineapple pure with LBG

c (%)	Frenkel-Eyring Equation	r	E_a kJ/mol
0.2	$\ln\eta_{(T)} = 1945.9/T - 7.9046$ $\eta(T) = 0.000369 \exp(1945.9/T^*)$	0.895	16178
0.4	$\ln\eta_{(T)} = 2424.8/T - 8.9615$ $\eta(T) = 0.000128 \exp(2424.8/T^*)$	0.993	20159
0.6	$\ln\eta_{(T)} = 2306.8/T - 8.1327$ $\eta(T) = 0.000294 \exp(2306.8/T^*)$	0.989	19178
0.8	$\ln\eta_{(T)} = 1502.4/T - 5.0707$ $\eta(T) = 0.006282 \exp(1502.4/T^*)$	0.939	12490
1	$\ln\eta_{(T)} = 1319.5/T - 4.2739$ $\eta(T) = 0.011413 \exp(1319.5/T^*)$	0.982	10970

7.4 Examination of material science for pineapple puree with guar gum

Normally pineapple puree has a problem with serum separation during storage and shear effect, due to the structure of puree was destroyed. The pineapple puree used guar gum in order to stabilize the structure of pineapple puree. Guar gum is one of widely use as stabilizer in galactomannan group. The objective of this study was to investigate the ability of guar gum to stabilize the structure of puree. To studied some factor, such as concentration and temperature, of pineapple puree with guar gum. The stability was measured by using the rheological method, such as shear rate examination and oscillation test. The parameter of result was analyzed by using Herschel-Bulkley and Ostwald-de Waele models.

7.4.1 Effect of concentration of guar gum on pineapple puree

Concentration was the one of importance effect on puree application. The proper concentration should suit the application the product is used for. To study the effect of concentration, guar gum at different concentration, such as 0.2, 0.4, 0.6, 0.8 and 1 %, was added to pineapple puree. The rheological method was used for measurement that shear rate examination ($0.1 < \dot{\gamma} < 50$) and oscillation test (Frequency sweep)

7.4.1.1 Shear rate examination

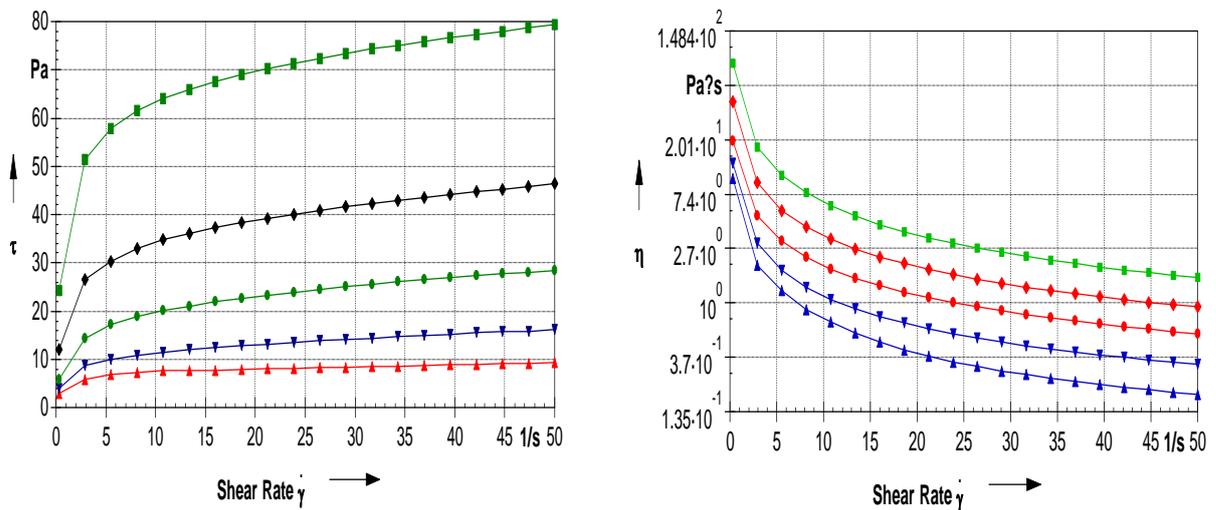


Figure 7.18 CSR-Examination for pineapple puree with different concentration of guar gum; 0.2 % (▲), 0.4 % (▼), 0.6 % (●), 0.8 % (◆) and 1% (■)

Table 7.9 Rheological parameters for effect of guar gum concentration on pineapple puree

c %	OW					HB						
	K Pa·s ⁿ	n	r	η_{eff} (50/s) Pa·s	τ_0 Pa	K Pa·s ⁿ	n	r	A_{TH} Pa·s ⁻¹	η_{eff} (50/s) Pa·s		
0	0.201	0.672	0.996	0.044	-	0.66	0.162	0.690	0.996	222	0.046	✓
0.2	11.38	0.157	0.968	0.235	✓	-2.80	24	0.09	0.993	21.43	0.337	-
0.4	12.96	0.208	0.991	0.338	✓	-12.97	25	0.109	0.998	21.97	0.285	-
0.6	14.54	0.243	0.999	0.445	✓	-23.37	30	0.121	0.999	22.99	0.302	-
0.8	18.03	0.259	0.984	0.595	✓	-180.86	100	0.169	0.999	45.63	0.373	-
1	24.75	0.295	0.968	0.963	✓	-1,924	920	0.171	0.98	48.63	0.980	-

Result on table 7.9 and figure 7.18 showed that the pineapple puree after adding guar gum exhibited a negative yield point (τ_0) compared with puree without gum. The pineapple puree with added guar gum performed the negative value at all range of concentration (0.2 to

1 %) Yield point performed an increasing trend on concentration. Therefore, rheological parameters matched the Ostwald-de Weale model. Its r value was more than 0.960 at all range of concentration. This can explained the behavior of pineapple puree in changing from fluid behavior to non-Newtonian fluid behavior with a strong decreasing of n after adding guar gum. The changing of parameters base on Ostwald-de Waele model showed that consistency factor (K) increased with concentration. The flow index increased with concentration adding. Therefore the stability of pineapple puree was reduced when guar gum was added higher concentration. The viscosity of guar gum was increased with concentration. To conclusion, the low concentration (0.2 %) showed the good potential to be the stabilizer for pineapple puree, because it was able to stabilize the structure of pineapple effectively. Adding guar gum did not impact on the viscosity of pineapple puree. It was only necessary to increase the stability of the pineapple puree.

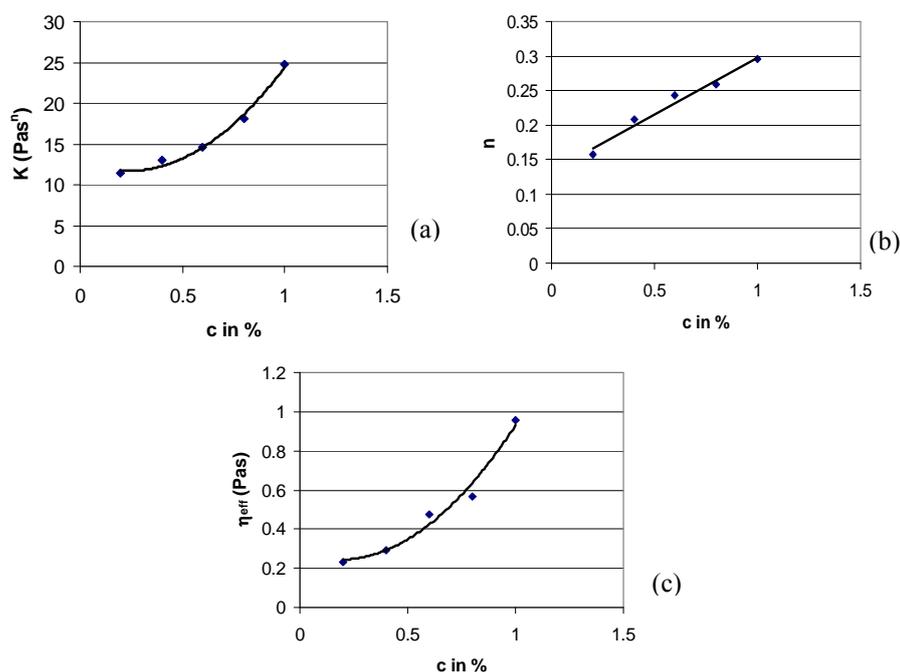


Figure 7.19 Trend diagrams of rheological parameters for effect of guar gum concentration on pineapple puree; Consistency factor (a), flow index (b) and Viscosity (c)

Trends of parameters for effect of guar gum on pineapple puree (Figure 7.19) showed that consistency factor (K) exhibited an increased trend with concentration. The predicted diagram matched the polynomial equation. (Eq. 7.14) The diagram of flow index (n) showed the highest value at 0.6 % of concentration and lowest value at 0.2 % of concentration. The predicted trend matched the polynomial equation. The viscosity diagram (η_{eff}) was increased with concentration. The predicted diagram matched the polynomial equation. (Eq. 7.15)

$$K(c) = 21.78 c_{gg}^2 - 10.228 c_{gg} + 12.889 \quad \text{in Pa}\cdot\text{s}^n \quad r = 0.988 \quad (\text{Eq. 7.14})$$

$$n(c) = 0.1635 c_{gg} + 0.1343 \quad r = 0.984 \quad (\text{Eq. 7.15})$$

$$\eta_{eff}(c) = 1.0214 \cdot c_{gg}^2 - 0.3667 \cdot c_{gg} + 0.276 \quad \text{in Pa}\cdot\text{s} \quad r = 0.987 \quad (\text{Eq. 7.16})$$

*Validity: $0.1 \leq \dot{\gamma} \leq 50$ 1/s and $0.2 \leq c_{gg} \leq 1$ %

7.4.1.2 Oscillation test

The microstructure of pineapple with guar gum was measured by using the oscillation test; frequency sweep method from 0.01 to 10 Hz. The behavior of pineapple puree was described by storage modulus (G') and $\tan \delta$.

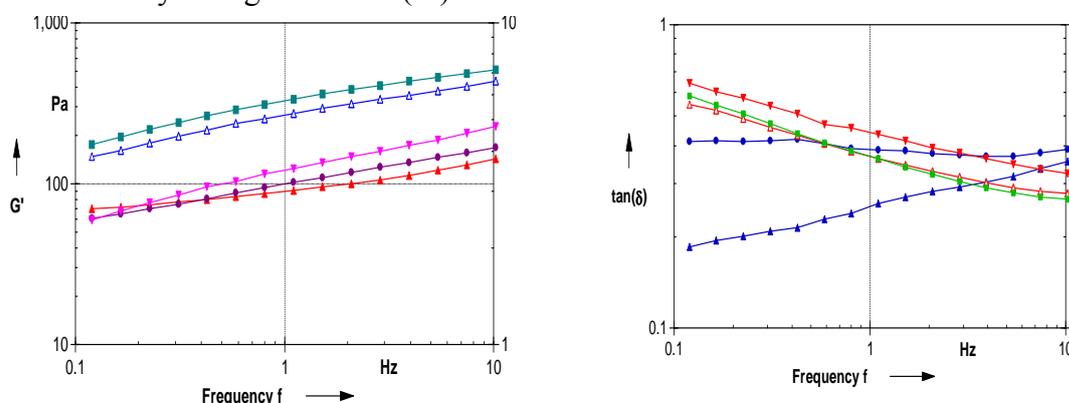


Figure 7.20 Frequency sweep diagram for pineapple puree with different concentration of guar gum; 0.2 % (\blacktriangle), 0.4 % (\bullet), 0.6 % (\blacktriangledown), 0.8 % (\triangle) and 1 % (\blacksquare)

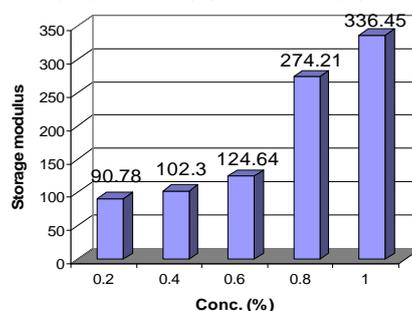


Figure 7.21 Storage modulus (G') for pineapple puree with different concentration of guar gum at 1 Hz of frequency

Results showed that storage modulus was higher than loss modulus at all range of frequency and all range of concentration. (Figure 7.20) It can be explained that the pineapple puree with guar gum performed the semi-solid behavior with particle dispersion. Comparison of storage modulus at frequency of 1 Hz (Figure 7.21), the storage modulus exhibited increasing with concentration. The G' increased dramatically after adding guar gum more than 0.8 %. This can be described the pineapple puree with high concentration performed more semi-solid like than low concentration.

7.4.2 Effect of temperature on pineapple puree with guar gum

The temperature of pineapple puree is one factor for identifying rheological properties, such as stability, viscosity properties. The aim of this study was to investigate the effect of temperature on pineapple puree with guar gum and relationship between concentration and temperature on rheological properties of puree with guar gum. The pineapple puree at different concentration of guar gum was measured rheological measurement at different temperature: 20, 30, 40, 50 and 60 °C. The rheological measurement used control shear rate examination ($0.1 < \dot{\gamma} < 50/s$).

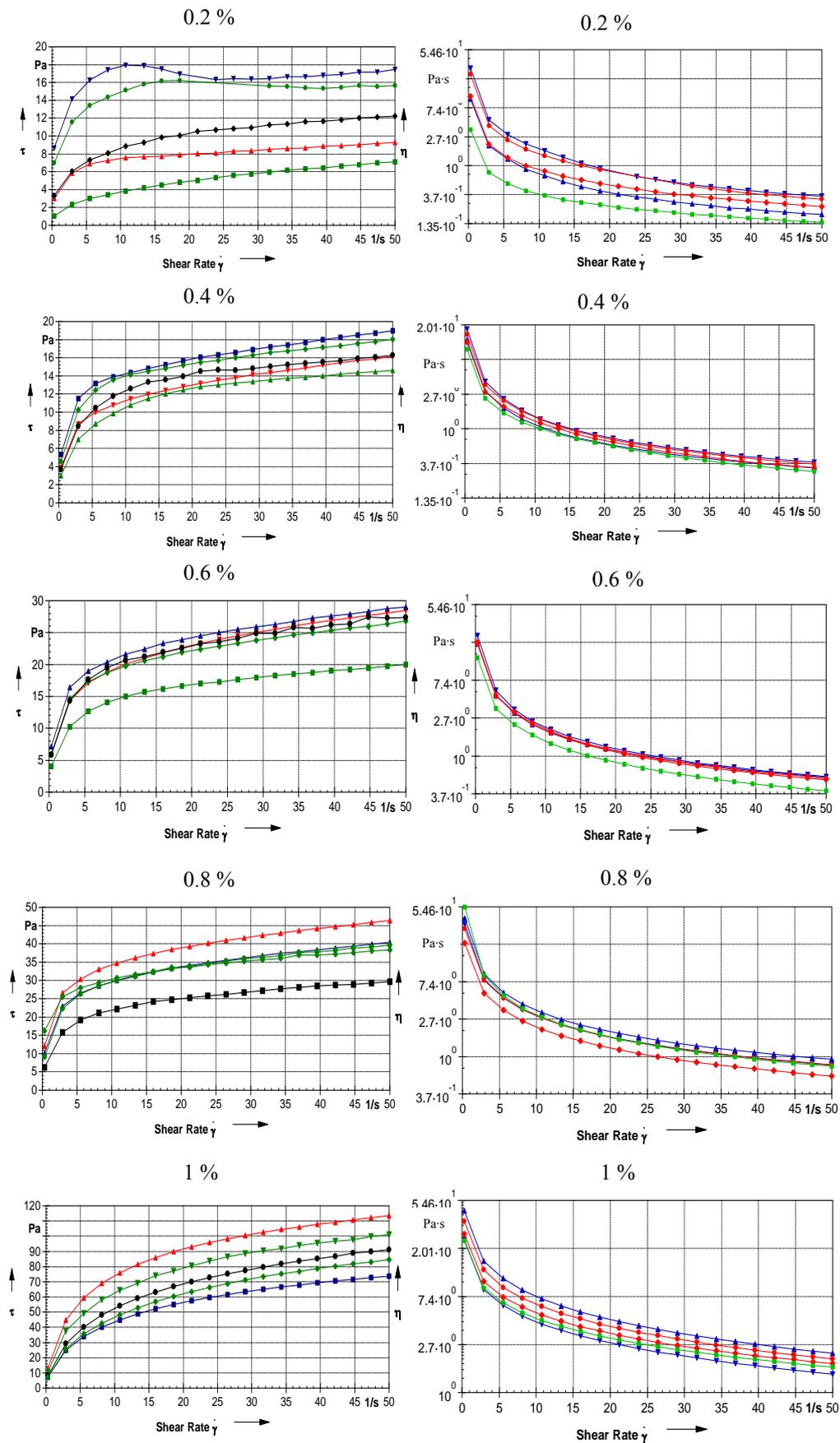


Figure 7.22 CSR-Examination for pineapple puree with different concentration of guar gum and temperature; 20 °C (▲), 30 °C (▼), 40 °C (●), 50 °C (◆) and 60 °C (■)

$$K(c,t) = 8.0513 + 22.7171 \cdot c_{gg} - 0.2067 \cdot t \quad \text{in Pa} \cdot \text{s}^n \quad r = 0.945 \quad (\text{Eq. 7.17})$$

$$n(c,t) = 0.0558 + 0.6315 \cdot c_{gg} + (8.7429 \cdot 10^{-5}) \cdot t - 0.4204 \cdot c_{gg}^2 - 0.0028 \cdot c_{gg} \cdot t + (3.257 \cdot 10^{-5}) \cdot t^2$$

$$r = 0.956 \quad (\text{Eq. 7.18})$$

$$\eta_{\text{eff}}(c,t) = 0.1943 + 0.6789 \cdot c_{gg} - 0.0049 \cdot t \quad \text{in Pa} \cdot \text{s} \quad r = 0.987 \quad (\text{Eq. 7.19})$$

*Validity: $20 \leq t \leq 60$ °C and $0.2 \leq c_{gg} \leq 1$ %

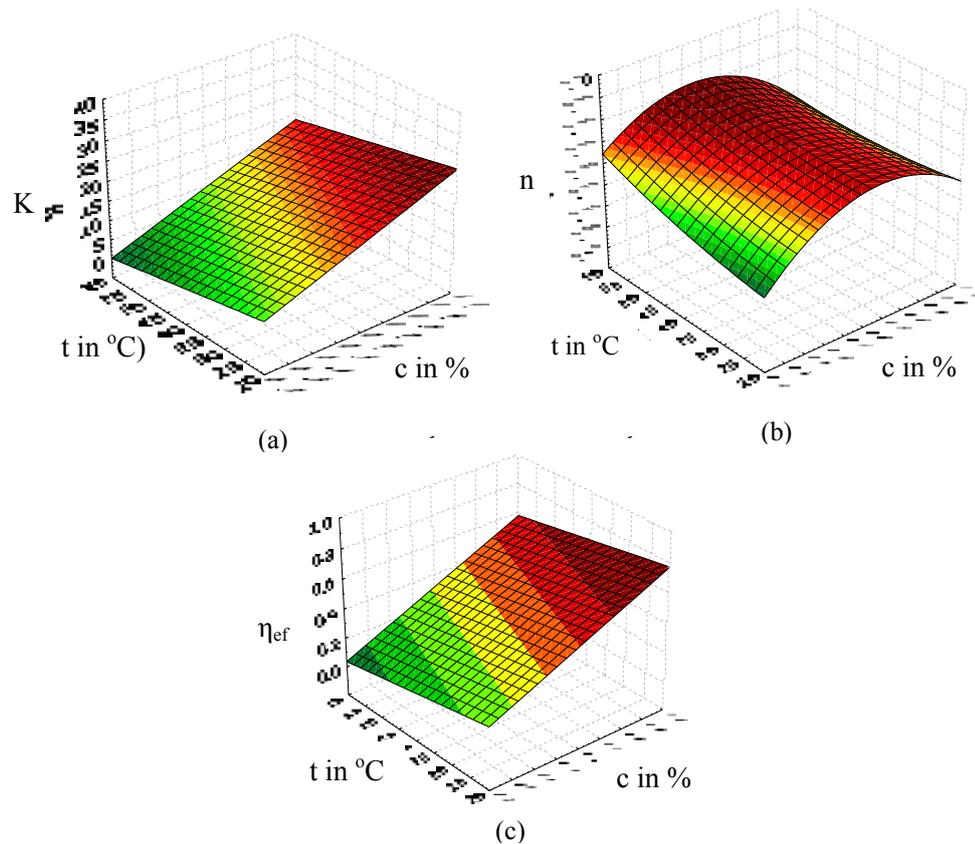


Figure 7.23 RSM diagrams of rheological parameters for effect of concentration and temperature on pineapple puree with guar gum; Consistency factor (a), Flow index (b) and Viscosity (c)

The flows activate energy or E_a was described by Frenkel-Eyring equation. (Table 7.11) The E_a was decreased with concentration of guar gum. Thus, the high concentration was used the less energy to overcome the barrier of flow. The pineapple puree with 0.2 % of concentration was increased significantly at 24.82 kJ/mol compare with 0.4 % of guar gum concentration.

Table 7.11 Flow activate energy for temperature changing of pineapple pure with guar gum

c %	Frenkel-Eyring Equation	r	E _a kJ/kmol
0.2	$\ln\eta_{(T)} = 2983.6/T - 11.378$ $\eta(T) = (1.14 \cdot 10^{-5})(2983.6/T^*)$	0.835	24805
0.4	$\ln\eta_{(T)} = 1463.6/T - 6.127$ $\eta(T) = 0.0021(1463.6/T^*)$	0.975	12168
0.6	$\ln\eta_{(T)} = 1131.3/T - 4.575$ $\eta(T) = 0.010(1131.3/T^*)$	0.928	9405
0.8	$\ln\eta_{(T)} = 845.52/T - 3.4508$ $\eta(T) = 0.031(845.52/T^*)$	0.892	7029
1	$\ln\eta_{(T)} = 1066.7/T - 3.7294$ $\eta(T) = 0.024(1066.7/T^*)$	0.964	8868

Choi & Yoo (2006) studied the rheological effect of gum addition to hot pepper-soybean pastes. (HPSP) Guar gum was used for improving its texture properties and controlling the rheological properties of products. Guar gum was added in HPSP at 0.5 % of concentration. Results showed that the flow index of HPSP after adding guar gum was indicated the extent of shear-thinning behavior. The temperature effect on viscosity was described well by the Frenkel-Eyring Equation with high correlations. (r) Base on Oscillation test, results showed the G' was higher than G'' .

7.5 Examination of material science for pineapple puree with xanthan gum

The xanthan gum was the one of animal stabilizers widely applied in many kind of semi-solid food, such as mayonnaise, whipped cream and fruit filling. However, xanthan gum has a highly cost compare plant gum. This study investigated the stability activity of xanthan gum in pineapple puree by examining the some factor on pineapple puree with xanthan gum, such as concentration of xanthan gum or effect of temperature. The study also investigated the rheological properties in the relationship between concentration and temperature. The rheological properties were used control shear rate examination and oscillation test for determining the stability and viscosity.

7.5.1 Effect of xanthan concentration on pineapple puree

To study the effect of concentration on pineapple puree, xanthan gum was added to pineapple puree at different concentration, such as 0.2, 0.4, 0.6, 0.8, 1 %. The stability and viscosity of pineapple puree with xanthan gum was determined by using rheological method: shear rate examination and oscillation test. (Frequency sweep) The Herschel-Bulkley and Ostwald-de Waele models were used for matching the rheological parameters and diagrams.

7.5.1.1 Shear rate examination

To study the structure of effect of xanthan gum on pineapple puree, the shear rate was used for investigating the macrostructure. This method used the shear rate at $0.1 \leq \dot{\gamma} \leq 50/s$ with five phase of measurement. The parameters were calculated from fifth phase of diagram and matched to the Herschel-Bulkley and Ostwald-de Waele models.

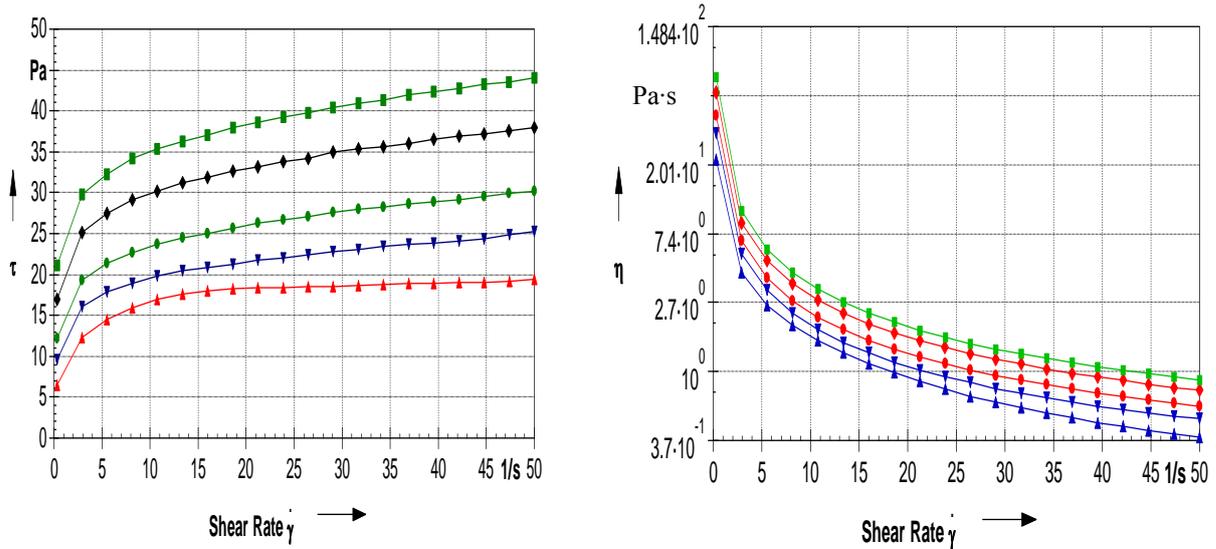


Figure 7.24 CSR-Examination for pineapple puree with different concentration of xanthan gum; 0.2 % (▲), 0.4 % (▼), 0.6 % (●), 0.8 % (◆) and 1% (■)

Table 7.12 Rheological parameters for effect of xanthan gum concentration on pineapple puree

c %	OW					HB						
	K Pa·s ⁿ	n	r	η_{eff} (50/s) Pa·s	τ_0 Pa	K Pa·s ⁿ	n	r	A_{TH} Pa·s ⁻¹	η_{eff} (50/s) Pa·s		
0	0.201	0.672	0.996	0.044	-	0.66	0.162	0.690	0.996	222	0.046	√
0.2	9.64	0.197	0.935	0.238	√	-250	260	0.01	0.958	14.	0.220	-
0.4	12.63	0.177	0.993	0.285	√	-47	59	0.046	0.998	8.8	0.269	-
0.6	15.58	0.170	0.997	0.341	√	-18	33	0.089	0.999	3.0	0.328	-
0.8	21.87	0.152	0.999	0.440	√	-11.	32	0.106	0.999	5.0	0.413	-
1	27.46	0.144	0.999	0.533	√	-4	29	0.122	0.999	15.1	0.477	-

Results showed that rheological parameters (Table 7.12) matched the Ostwald-de Waele model because yield point (τ_0) of Herschel-Bulkley model showed negative value. Thus, Herschel-Bulkley model was invalid for fitting parameters. Comparing with pure pineapple puree and pineapple puree with xanthan gum, pineapple puree with xanthan gum exhibited a positive value of yield point which changed to negative value when xanthan gum was added. Therefore, the xanthan changed the behavior of pineapple puree from fluid behavior to non-Newtonian with highly viscous liquid. However, the yield point showed the increasing trend when the concentration was increased. Thus, the behavior of pineapple puree with xanthan gum performed the more fluid behavior when xanthan concentration was increased. It may show the fluid behavior at higher 1 % of concentration.

The effect of concentration on other parameters base on Ostwald-de Waele model showed that consistency factor (K) increased with increasing concentration. The flow index (n) exhibited the decreasing trend with increasing concentration. Thus, xanthan gum was able to stabilize the structure of pineapple puree at high concentration better than low concentration. Viscosity was increased with concentration. Therefore, xanthan gum was able to induce both of stability and viscosity properties of pineapple puree. Zhao *et. al.* (2009) studied effect of xanthan adding in whipped cream. Xanthan gum showed the good result of stabilizes the structure of whipped cream.

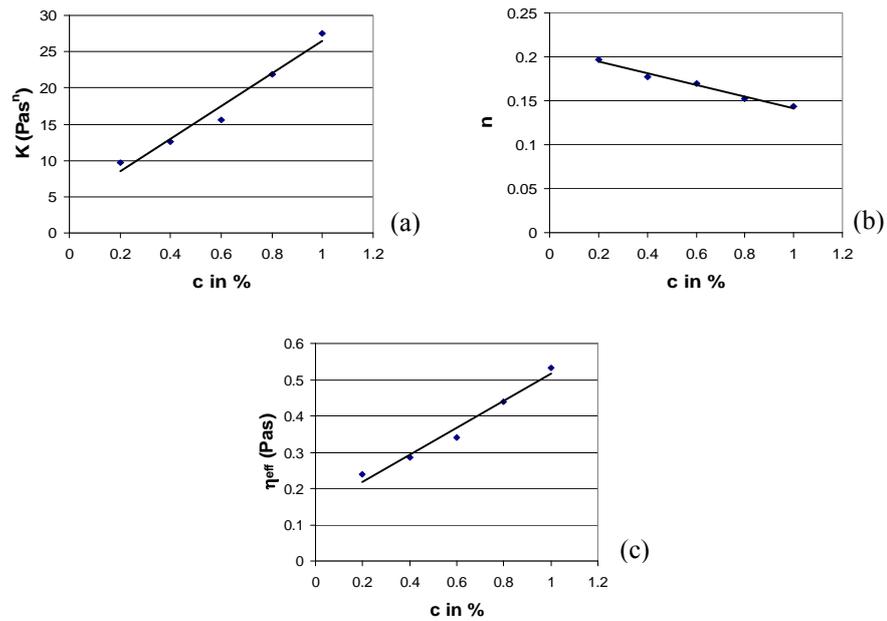


Figure 7.25 Trend diagrams of rheological parameters for effect of xanthan gum concentration on pineapple puree; Consistency factor (a), flow index (b) and Viscosity (c)

Trend diagrams of parameters (Figure 7.25) showed that the consistency factor (K) showed an increase with concentration. The trend curve matched the linear equation. (Eq. 7.20) The flow index (n) exhibited a decreasing trend with an increasing concentration. The trend curve was fitted with linear equation. (Eq. 7.21) The viscosity demonstrated the same as consistency factor trend: it increased with concentration. The trend curve matched the linear equation. (Eq. 7.22)

$$K(c) = 22.44 \cdot c_{xg} + 3.972 \quad \text{in Pa} \cdot \text{s}^n \quad r = 0.984 \quad (\text{Eq. 7.20})$$

$$n(c) = -0.0655 \cdot c_{xg} + 0.2073 \quad r = 0.987 \quad (\text{Eq. 7.21})$$

$$\eta_{\text{eff}}(c) = 0.3725 \cdot c_{xg} + 0.1439 \quad \text{in Pa} \cdot \text{s} \quad r = 0.987 \quad (\text{Eq. 7.22})$$

*Validity: $0.1 \leq \dot{\gamma} \leq 50/\text{s}$ and $0.2 \leq c_{xg} \leq 1\%$

7.5.1.2 Oscillation test

The effect of concentration on microstructure and viscoelasticity of pineapple puree with xanthan gum was determined by using an oscillation test with frequency sweep method at 0.01 to 10 Hz of frequency.

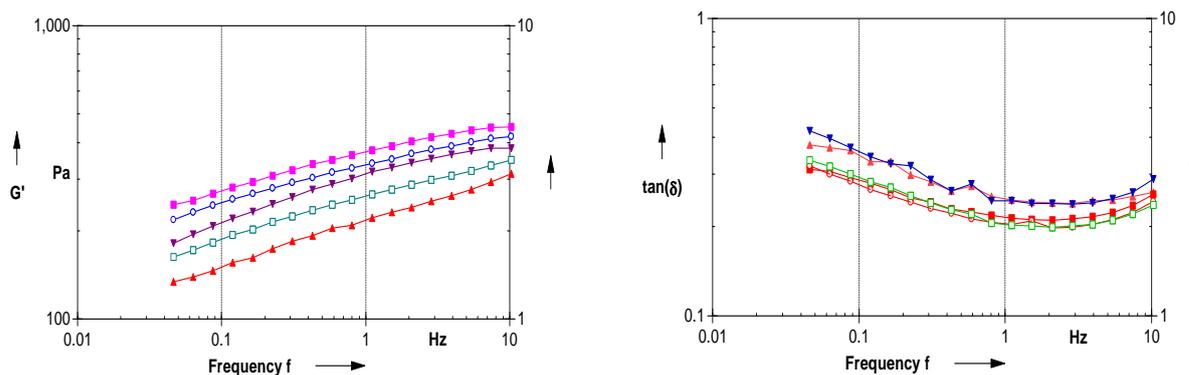


Figure 7.26 Oscillation diagrams (frequency sweep) for pineapple puree with different concentration of xanthan gum; 0.2 % (▲), 0.4 % (▼), 0.6 % (■), 0.8 % (○) and 1 % (□)

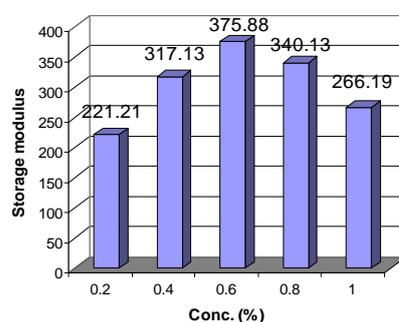


Figure 7.27 Storage modulus (G') for pineapple puree with different concentration of xanthan gum at 1 Hz of frequency

Results showed that storage modulus (G') was higher than loss modulus at all range of frequency. (Figure 7.26) The G' curve showed the slope. Therefore, pineapple puree with xanthan gum performed semi-solid behavior with particle dispersion system. However, highest value of G' was at 0.6 % of concentration, according to figure 7.27. Thus, pineapple puree at 0.6 % concentration of xanthan gum performed greater semi-solid behavior than other level concentration of xanthan gum. In contrast, the 0.2 and 1 % of concentration showed more the fluid like behavior, but it still to be the semi-solid behavior.

7.5.2 Effect of temperature on pineapple puree with xanthan gum

Temperature was one of identified parameters for determining the rheological properties for pineapple puree. Normally, the rheological properties were changed by temperature. The aim of this study was to study the effect of proper temperature on pineapple puree with added xanthan gum. The pineapple puree with added xanthan was measured the rheological properties, such as shear rate examination at different level of temperature. (20, 30, 40, 50 and 60 °C) Furthermore, the relationship between concentration and temperature on rheological properties also investigated by using RSM methods.

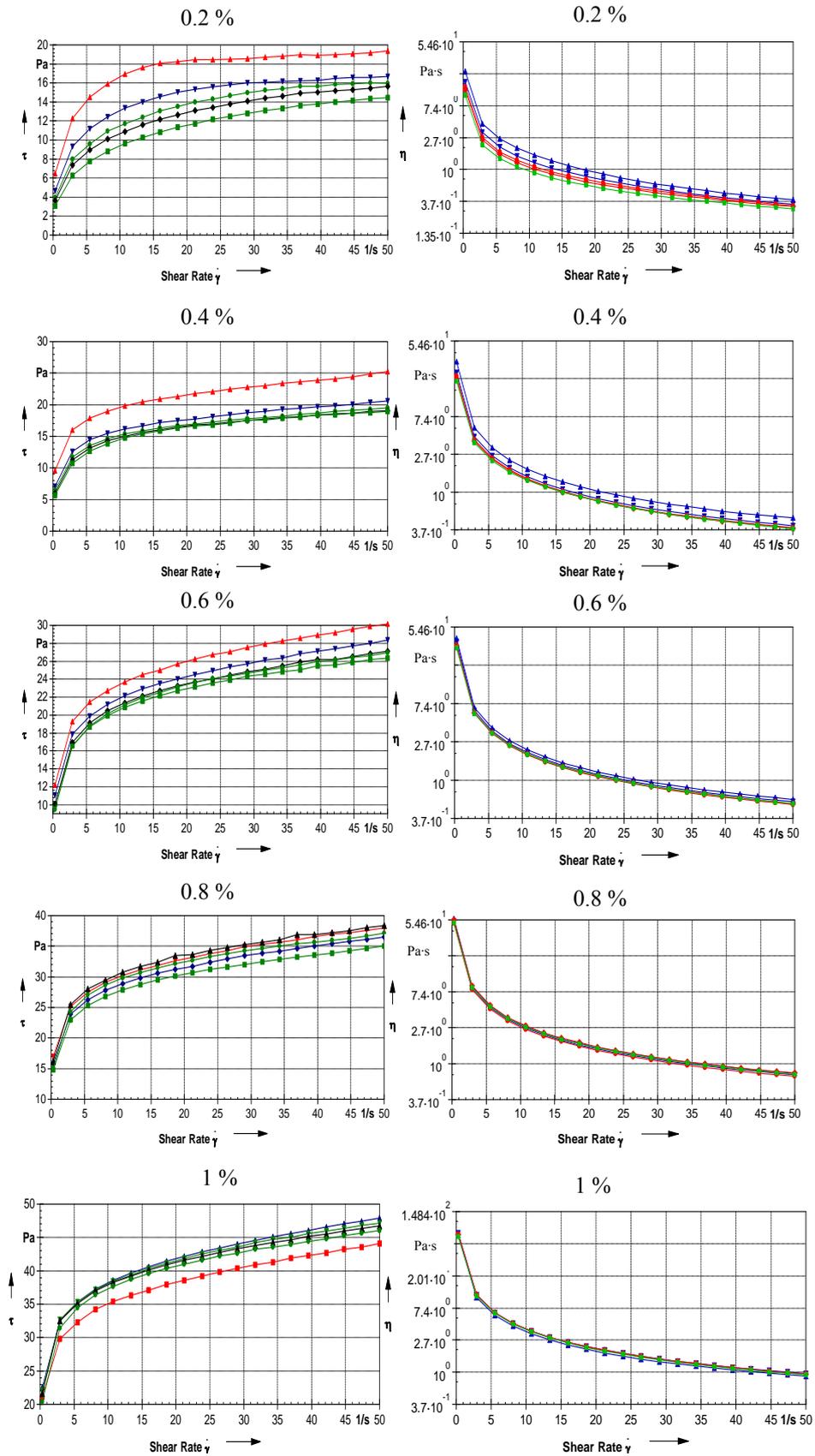


Figure 7.28 CSR-Examination for pineapple puree with different concentration of xanthan gum and temperature; 20 °C (▲), 30 °C (▼), 40 °C (●), 50 °C (◆) and 60 °C (■)

Table 7.13 Rheological parameters for effect of temperature on pineapple puree with xanthan gum

<i>C</i> %	<i>t</i> ₂₀	<i>t</i> ₆₀	ΔK^* (20-60 °C) <i>Pa·sⁿ</i>	Δn^* (20-60 °C) -	$\Delta \eta_{eff} (50/s)^*$ (20-60 °C) <i>Pa·s</i>		
0.2	OW	OW	5.047	(-) 0.101	0.0576		
						n : 0.197	n : 0.298
						K : 9.64	K : 4.593
						r : 0.935	r : 0.993
0.4	OW	OW	4.493	(-) 0.045	0.0592		
						η_{eff} : 0.238	η_{eff} : 0.181
						n : 0.177	n : 0.222
						K : 12.63	K : 8.141
0.6	OW	OW	3.523	(-) 0.032	0.0352		
						r : 0.993	r : 0.981
						η_{eff} : 0.285	η_{eff} : 0.226
						n : 0.170	n : 0.202
0.8	OW	OW	3.814	(-) 0.012	0.0561		
						K : 15.58	K : 12.066
						r : 0.997	r : 0.933
						η_{eff} : 0.341	η_{eff} : 0.305
1	OW	OW	1.112	(-) 0.002	0.0169		
						n : 0.152	n : 0.164
						K : 21.87	K : 18.062
						r : 0.999	r : 0.983
	OW	OW					
						η_{eff} : 0.440	η_{eff} : 0.384
						n : 0.144	n : 0.146
						K : 27.46	K : 26.35
	OW	OW					
						r : 0.999	r : 0.996
						η_{eff} : 0.533	η_{eff} : 0.516

*Calculation of parameters difference was based on Ostwald-de Waele model

Results (Table 7.13) showed that rheological parameters matched Ostwald-de Waele model closely at all range of concentration and temperature, because the yield point (τ_0) performed negative value. Thus, the behavior of pineapple puree with xanthan gum showed the same behavior at all level of temperature which exhibited the semi-solid behavior. Difference of consistency factor (ΔK) showed a positive value at all ranges of concentration. This is because the K value decreased with temperature. Moreover, ΔK showed increasing trends with concentration. The K parameters of pineapple puree with xanthan gum at low concentration were more influence by temperature than at high concentration. Difference of flow index (Δn) showed negative value, so the flow index (n) increased with temperature. It can be described that stability of pineapple puree structure was loss with increasing temperature. Difference of viscosity ($\Delta \eta_{eff}$) showed positive value, so the viscosity was decreased with temperature. The $\Delta \eta_{eff}$ exhibited non-identifiable trend with concentration, whereas the high value of $\Delta \eta_{eff}$ was at 0.2 and 0.4 % of xanthan concentration. Therefore, pineapple puree with low concentration of xanthan gum was more influence on decreasing viscosity than xanthan gum at high concentration, because the high temperature destroyed a blinding structure between puree and xanthan. In addition, the temperature destroyed the cell of pineapple resulting in more serum in system.

However, the pineapple puree with added xanthan gum of all level concentration showed the small changing value of viscosity and flow index. (less than 0.1) This can be explained that xanthan was made the strong structure on pineapple puree. Therefore pineapple puree with added xanthan gum has good temperature resistance.

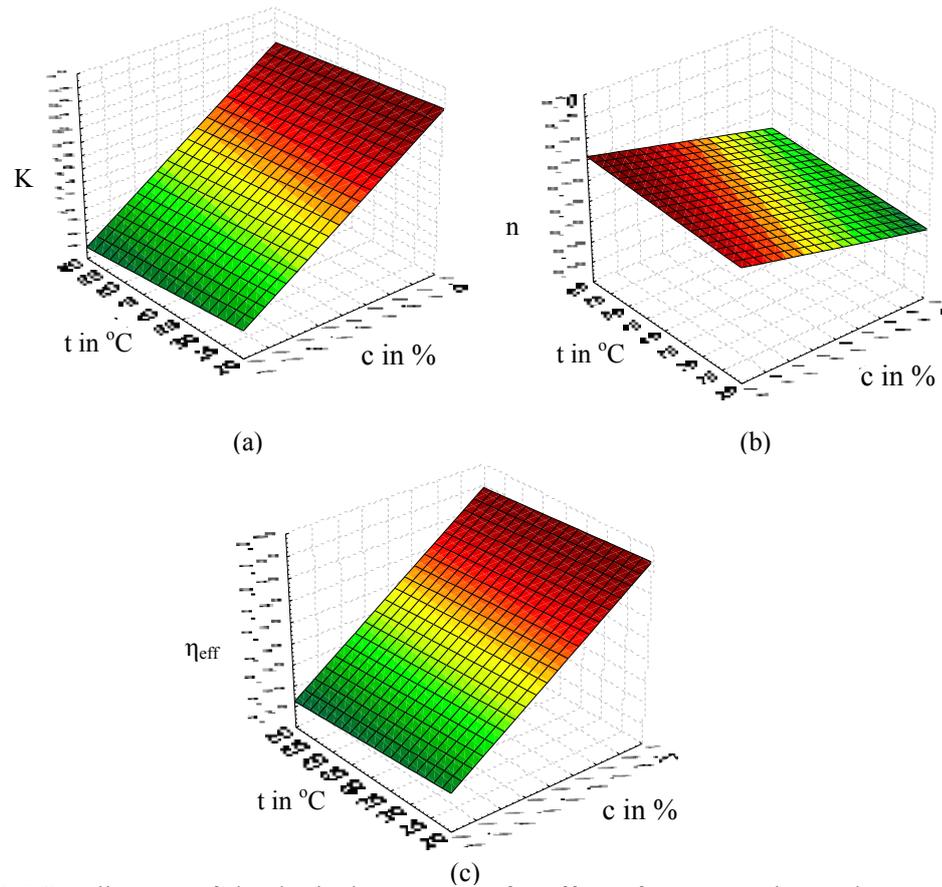


Figure 7.29 RSM diagram of rheological parameters for effect of concentration and temperature on pineapple puree with xanthan; consistency factor (a), flow index (b) and viscosity (c)

Predicted lines between concentration and temperature of pineapple puree with xanthan gum (figure 7.29) showed that consistency factor (K) increased with concentration and decreased with increasing temperature. The trend diagram matched the linear equation. (Eq. 7.23) Flow index (n) was decreased with concentration and increased with temperature. The trend diagram matched the linear equation. (Eq. 7.24) Viscosity parameter (η_{eff}) increased with concentration and decreased with temperature. The trend diagram matched the linear equation. (Eq. 7.25)

$$K(c, t) = 2.3669 + 25.945 \cdot c_{\text{xg}} - 0.062 \cdot t \quad \text{in Pa} \cdot \text{s}^n \quad r = 0.993 \quad (\text{Eq. 7.23})$$

$$n(c, t) = 0.2334 - 0.1304 \cdot c_{\text{xg}} + 0.0008 \cdot t \quad r = 0.961 \quad (\text{Eq. 7.24})$$

$$\eta_{\text{eff}}(c, t) = 0.122 + 0.4141 \cdot c_{\text{xg}} - 0.0007 \cdot t \quad \text{in Pa} \cdot \text{s} \quad r = 0.990 \quad (\text{Eq. 7.25})$$

*Validity: $20 \leq t \leq 60$ °C and $0.2 \leq c_{\text{xg}} \leq 1$ %

Flows activation energy or E_a (Table 7.14) was calculated base on viscosity of pineapple puree with xanthan gum at temperature from 20 to 60 °C in Ostwald-de Waele model. The E_a was described by Frenkel-Eyring Equation. The E_a showed that pineapple puree with low concentration of xanthan gum (0.2 and 0.4 %) exhibited significantly higher value of E_a than high concentration.

Table 7.14 Flow activate energy for temperature changing of pineapple pure with xanthan

c %	Frenkel-Eyring Equation	r	E _a kJ/mol
0.2	$\ln\eta_{(T)} = 600.66/T - 3.5232$ $\eta(T) = 0.029 \exp(600.66/T^*)$	0.938	24805
0.4	$\ln\eta_{(T)} = 528.44/T - 3.1191$ $\eta(T) = 0.044 \exp(528.44/T^*)$	0.847	12168
0.6	$\ln\eta_{(T)} = 249.23/T - 1.9328$ $\eta(T) = 0.144 \exp(249.23/T^*)$	0.928	2072
0.8	$\ln\eta_{(T)} = 356.94/T - 2.0208$ $\eta(T) = 0.132 \exp(356.94/T^*)$	0.892	2967
1	$\ln\eta_{(T)} = 81.653/T - 0.9037$ $\eta(T) = 0.405 \exp(81.653/T^*)$	0.942	678

7.6 Interaction between galactomannan and xanthan gum in pineapple puree

Properties of xanthan can be improved by synergic with galactomannan, such as guar gum and locust bean gum. In this study, the mixing gums were added to pineapple puree in order to improve the stability of pineapple puree structure. The objective of the study was investigated the synergistic between galactomannan and xanthan gum. Mixed gums were added to pineapple puree at different ratio of galactomannan and xanthan , such as 100:0, 85:15, 75:25, 50:50, 25:75, 15:85 and 0:100. The rheological method was used to study the stability properties of mixed gums in pineapple puree by using control shear rate examination and oscillation.

7.6.1 Shear rate examination

The shear rate examination revealed the macro-structure of pineapple puree with interaction between galactomannan and xanthan by using shear rate $\dot{\gamma}$ up to 50/s.

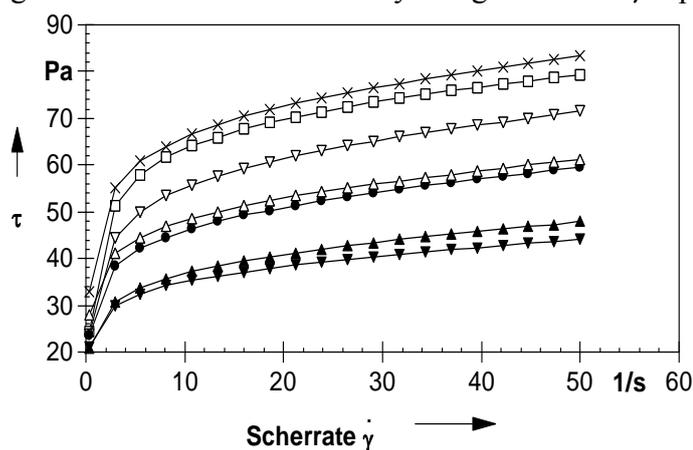


Figure 7.30 CSR-Examination for effect of ratio between guar and xanthan gum; 100:0 (\square), 85:15 (\circ), 75:25 (\times), 50:50 (\bullet), 25:75 (Δ), 15:85 (\blacktriangle) and 0:100 (\blacktriangledown)

Table 7.15 Rheological parameters for pineapple puree with mixing gums

<i>Gum added</i>	<i>OW</i>					<i>HB</i>					
	K Pa·s ⁿ	n	r	s Pa	η_{eff} (50/s) Pa·s	τ_0 Pa	K Pa·s ⁿ	n	r	s Pa	η_{eff} (50/s) Pa·s
Guar : XG											
0 : 100	25.2	0.140	0.999	0.20	0.873	-4	29.79	0.122	0.999	0.2	0.873
15 : 85	25.2	0.167	0.986	1.00	0.969	-3	28.49	0.146	0.998	0.22	0.948
25 : 75	31.5	0.167	0.998	0.40	1.211	-12	46.50	0.114	0.998	0.39	1.207
50 : 50	32.8	0.172	0.982	1.480	1.210	-43	73.749	0.082	0.998	0.388	1.171
75 : 25	43.3	0.170	0.992	1.475	1.688	-183	225.160	0.024	0.999	0.460	1.617
85 : 15	34.7	0.192	0.971	2.401	1.475	-251	285.73	0.030	0.999	0.355	1.398
100 : 0	36.7	0.288	0.970	13.17	0.958	-1024	1062.5	0.010	0.949	0.48	0.568
LBG : XG											
50 : 50	65.26	0.850	0.902	4.02	1.82	65.60	1.48	0.787	0.999	0.48	1.954

Results showed (Table 7.15, Figure 7.30) that rheological parameter of interaction between guar gum and xanthan gum matched the Ostwald-de Waele model closely, because the yield point exhibited a negative value. Combination between LBG and xanthan gum (50:50) showed good matching with Herschel Bulkley model, because yield point exhibited positive value. It can be explained that the pineapple puree with xanthan gum and locust bean gum exhibited a gel behavior instead of semi-solid behavior due to the yield point exhibiting high positive value. In contrast, the combination of xanthan and guar gum exhibited the semisolid with shear thinning behavior. However, the aim of adding gum was to improve the stability of pineapple puree and retain the behavior as the behavior as a semisolid. In this study, therefore, the interaction between guar and xanthan was emphasized to investigate the rheological properties.

Result of interactions between guar and xanthan gum showed that consistency factor (K) increased until 75 % of guar gum fraction. Flow index (n) increased with guar gum fraction, so the stability of pineapple puree was reduced with guar gum fraction. Viscosity was increased when guar gum added with xanthan gum to pineapple puree. It can be explained that guar gum fraction reduced the stability improvement, but it was able to enhance the viscosity of pineapple puree. Therefore, the synergistic between guar and xanthan only enhanced the viscosity in pineapple puree.

7.5.2 Oscillation test

The oscillation test investigated the micro-structure of pineapple puree and the interaction between galactomannan and xanthan gum. Results showed that storage modulus (G') was higher than loss modulus (G'') at all range of frequency ($0.1 \leq f \leq 10$ Hz.) Therefore, pineapple puree with xanthan and guar gum exhibited the semi-solid state with particle dispersion. According to Figure 7.31, G' was highest at ratio of 50:50. Thus, pineapple puree at this ratio was more fluid-like than at other ratio of xanthan and guar gum. Furthermore, the diagram of G' and frequency exhibited a slope. Therefore, the pineapple puree containing xanthan and guar gum performed a particle gel networks.

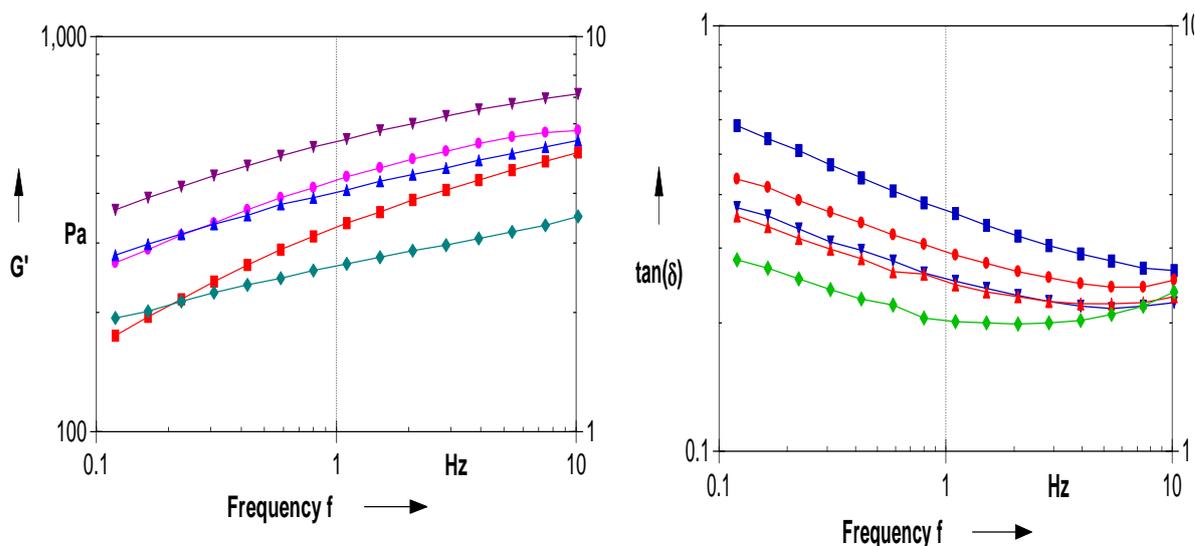


Figure 7.31 Oscillation diagram (Frequency sweep) for effect of interaction between galactomannan and xanthan gum; 100:0 (■), 75:25 (●), 50:50 (▼), 25:75 (▲) and 0:100 (◆)

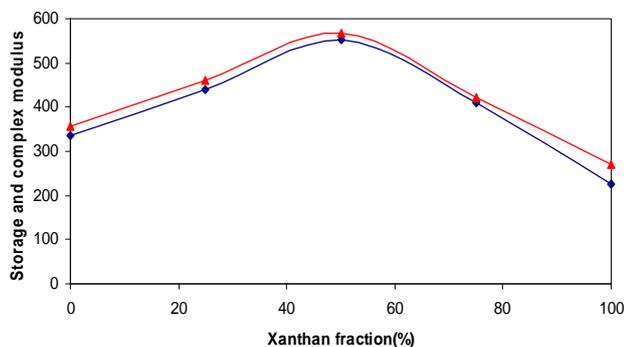


Figure 7.32 Storage modulus for interaction between guar and xanthan; G' (◆) and $[G^*]$ (▲)

7.7 Particle size examination for pineapple puree with different stabilizer

Particle size measured the droplet size of pineapple puree with different stabilizers such as locust bean, guar and xanthan gum and concentration at 0.2, 0.4, 0.6, 0.8 and 1 %. Furthermore, the particle size of pineapple puree with mixed gums was measured by investigating the effect of ratio between guar gum and locust bean gum. This mixed pair showed the good stability of structure in pineapple puree, according to result of their rheological properties. The ratio between guar and xanthan gum applied in this study were 100:0, 75:25, 50:50, 25:75 and 0:100. The reflective index was 0.146 as same as emulsion sample.

Result showed (Table 7.16) that the effect of gums adding in pineapple puree did not show a great impact on particle size in the pineapple puree. It can be seen that the mean size of pineapple puree exhibited similar value of between 320 to 450 μm . Pineapple puree with locust bean gum showed decreased particle size with an increase in concentration. Pineapple puree with guar gum also showed the same trend as locust bean gum samples. In contrast, pineapple puree with xanthan gum exhibited the opposite trend of locust bean gum and guar gum: the mean size showed a decrease with increased concentration. In the case of mixed gums, pineapple puree exhibited non-identifiable trend of mean particle size. There was no

difference in mean size in pineapple puree with different ratio of gums. Thus, the ratio of mixing gum has no affect on particle size in pineapple puree. The concentration showed some effect on particle size of pineapple puree, but there was no significantly difference. The particle size had small changing on pineapple puree with different stabilizer. Therefore, pineapple puree composition has more effect on particle size than stabilizer composition.

In comparison between gums, the particle size of pineapple puree showed no different between different gums adding. The mean size of mixing gum samples was more or equal than xanthan gum. Xanthan gum was smaller than LBG, but LBG was smaller than guar gum. (Mixing gum \geq Xanthan $>$ LBG $>$ Guar) In case of specific area, guar gum was bigger than mixing gum. Mixing gum was bigger than xanthan gum and LBG. (Guar $>$ Mixing gum $>$ xanthan = LBG)

Table 7.16 Particle size of pineapple puree with different stabilizers

Samples	Mean size (μm)	Diameter (μm)			Mode size	S.P. area (cm^2/ml)
		d ₁₀	d ₅₀ (Median)	d ₉₀		
LBG						
0.2 %	396.76	152.3	452.5	826.5	482.1	203
0.4 %	388.71	147.7	446.9	823.7	481.5	203
0.6 %	341.75	131.9	392.8	723.6	420.8	250
0.8 %	332.56	128.4	373.2	669.9	420.4	263
1%	328.69	133.1	425.9	791.4	423.3	247
Guar gum						
0.2 %	322.61	128.0	434.9	687.0	369.1	248
0.4 %	349.35	119.4	376.5	704.6	367.5	269
0.6 %	352.69	118.8	333.3	668.3	367.6	306
0.8 %	377.22	106.9	339.0	669.6	368.7	296
1%	384.96	99.6	348.2	668.2	368.4	311
Xanthan						
0.2 %	414.83	157.4	473.3	482.9	482.9	196
0.4 %	397.50	151.8	453.3	482.5	482.5	204
0.6 %	389.66	147.0	440.7	422.9	422.9	210
0.8 %	384.63	156.1	471.9	483.7	483.7	196
1%	388.15	149.8	442.1	481.9	481.9	207
Guar : Xanthan						
100:0	442.1	149.8	338.1	802.0	481.9	206
75:25	456.3	150.1	395.1	848.0	481.5	205
50:50	448.5	121.1	372.3	879.4	423.2	239
25:75	416.7	108.4	357.5	800.4	481.2	271
0:100	461.8	108.2	384.9	925.4	483.7	259

Chapter 8 comparison between pineapple puree and commercial puree

The aim of this study was to compare pineapple puree (Final product) and commercial products. The commercial product was represented by two group of product: dessert food and baby food product. The dessert was represented by apple puree from Diatini and Odenwald, purchased from Reichet supermarket, Berlin, Germany. The baby food group was represented by pear puree (Bebivita band), purchased from Edeka supermarket. The biggest group found in Germany market, was the mixing fruits puree used as baby food. (Figure 8.1(a)) These groups were represented by banana in apple puree (HiPP), banana in apple (Bebivita), peach in apple (HiPP), peach in passion fruit (Bebivita) and fruit salad (HiPP). The samples were purchased from Rossman and Edeka supermarket. (Figure 8.1b) Pineapple puree was represented by pineapple with added guar and xanthan gum mixture in ratio of 15:85 (XG/GG) According to previous results, it showed the high viscosity and stability.

According to rheological results, pineapple puree product was represented by pineapple puree added with guar and xanthan gum mixing (15:85), because it exhibited high stability and viscosity compare with other stabilizer, such as guar, locust bean gum and pectin.



Figure 8.1 samples of apple puree product (a), samples of baby food product (b)

8.1 pH and total soluble solid (TTS) (°Brix)

To study the characteristic of selected commercial products and pineapple puree (Final product), the pH and TTS of the products was measured. (Table 8.1) The results showed that the products in apple purees group exhibited lower pH value than the baby food. However, overall pH of puree product was range from 3 to 4. Results of total soluble solid showed that there are no difference between 2 groups. (apple puree and baby food group) The total soluble solid ranged form 12 to 18 °Brix. Parpinello (2001) studied the browning reaction control of apple and pear puree. The initial properties were also included in the study. Results showed that the pH value of apple and pear puree was about 4.0 and 4.4 respectively. The total soluble solid of apple and pear puree were found to be 18 and 12.2 °Brix, respectively. In comparison between pineapple puree and the commercial products, pH and TTS of pineapple puree exhibited similar value to the commercial puree products.

Table 8.1 pH and total soluble solid of some selected commercial products

<i>Type of puree</i>	<i>pH</i>	<i>TTS (° Brix)</i>
Pineapple puree	4.16	14
Apple puree (Diatini)	3.54	12
Apple puree (Odenwald)	3.62	14
Banana in apple puree (Bebivita)	3.95	14
Banana in apple puree (HiPP)	4.14	15
Peace in passion fruit (Bebivita)	3.84	18
Peace in apple (HiPP)	3.99	16
Pear puree (Bebivita)	4.03	13
Fruit salad (HiPP)	3.82	18

8.2 Rheological properties of selected commercial products

To order to investigate the structure of selected products and compare with pineapple puree (Final product), the rheological methods were used to determine the flow and viscoelastic behavior: Control shear rate examination at several level of temperature and the oscillation test. (Frequency sweep, Amplitude sweep and temperature sweep)

8.2.1 Steady shear rate examination

the flow behavior of the commercial products were determined by using the Control shear rate examination method. This measurement was used the five phase method by increasing in shear rate up to 50/s. Parameters was calculated from fifth phase of diagrams. Herschel-Bulkley and Ostwald-de Waele model were used for matching rheological curves and parameters.

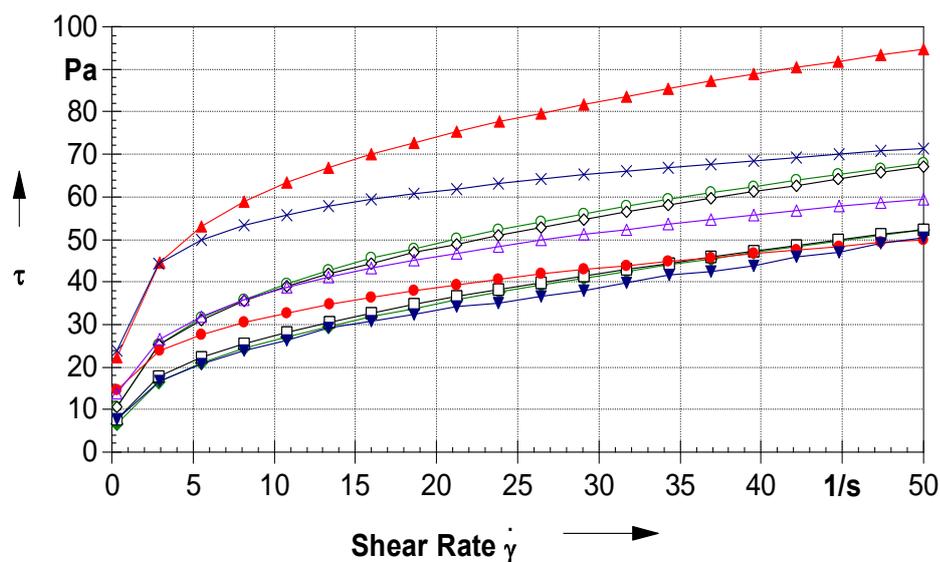


Figure 8.2 CSR-Examiantio for pineapple puree (x) and commercial puree products; Dietini (▲) and Odenwald (△), Banana in apple (bebevita) (○), Banana in apple (HiPP) (●), Pear (◇), Peach in Passion fruit (◆), Peach in apple (□) and Fruit salad (▼)

Table 8.2 Rheological parameter for selected commercial products

Type	OW					HB					
	K Pa·s ⁿ	n	r	η_{eff} (50/s) Pa·s	τ_0 Pa	K Pa·s ⁿ	n	r	η_{eff} (50/s) Pa·s		
Pineapple puree	30.80	0.172	0.982	1.210	√	-43	73.749	0.082	0.998	1.171	-
Apple puree (Dietini)	32.28	0.277	0.998	1.156	√	-10.06	42.60	0.228	0.999	1.117	-
Apple puree (Odenwald)	19.77	0.285	0.997	0.735	√	-1.44	21.00	0.272	0.999	0.720	-
Banana in apple (Bebivita)	16.78	0.368	0.982	0.914	√	-1.71	18.62	0.335	0.999	0.854	-
Banana in apple (HiPP)	18.53	0.255	0.992	0.600	-	6.26	12.32	0.322	0.999	0.606	√
pear (Bebivita)	16.61	0.368	0.983	0.905	√	-2.24	18.99	0.327	0.999	0.834	
Peach in passion fruit (Bebivita)	10.45	0.422	0.979	0.730	-	1.06	9.43	0.428	0.999	0.688	√
Peach in apple (HiPP)	11.91	0.388	0.983	0.711	-	1.09	10.63	0.397	0.999	0.673	√
Fruit salad (HiPP)	12.54	0.380	0.835	0.721	-	2.33	8.82	0.422	0.997	0.639	√

*(√) valid; (-) non-valid parameters

Results of apple purees group showed that both samples of apple puree matched the Ostwald de-Waele model closely, because yield point (τ_0) revealed the negative value. For flow index (n), both bands of apple puree showed the similar results of about 0.277 and 0.285. A consistency factor of apple puree (Dietini) was higher than apple puree (Odenwald). In case of viscosity, the apple puree from Odenwald was lower than apple puree from Dietini at 1.156 and 0.779 Pa·s. It can be described that the apple puree (Dietini) has stronger structure than apple puree (Odenwald). (Table8.2)

Results (Table 8.2) of baby food group showed that rheological parameter of banana in apple (Bebivita) and pear puree (Bebivita) matched the Ostwald-de Waele model. In contrast, banana in apple (HiPP), Peach in passion fruit (Bebivita), Peach in apple (HiPP) and fruit salad matched the Herschel-Bulkley model. For flow index (n), the banana in apple puree (HiPP) showed the lowest flow index. Therefore, banana puree (HiPP) have strong structure. In contrast, peach in passion fruit (Bebivita) showed the highest flow index compared with other samples about 0.428. However, overall flow index of fruit type baby food was range from 0.322 to 0.428. The viscosity of fruit type baby foods showed the similar value range from 0.639 to 0.854 Pa·s. The highest viscosity in baby food group was banana in apple from Bebevita at about 0.982 Pa·s. (OW)

In Comparison between the baby food group and apple puree group, the apple puree was more stable structure than the baby groups, because flow index exhibited low value. The viscosity of apple puree was higher than the baby food group as well. This is because the apple puree contains sugar as one of ingredient, but the baby contains sugar. Thus, sugar is able to enhance the viscosity. In this case of stability, starch was concerned to having effect in this property. Starch in baby food ingredient is able to enhance the stability of baby food. In other hand, apple puree contains only sugar. Thus, stability of baby was better than apple puree products.

From figure 8.2, the effect of shear rate (50/s) on two bands of apple puree showed that the flow behavior of apple puree two bands performed the shear thinning with yield behavior. The shear rate was greater effect with apple puree (Dietini) than apple puree (Odenwald). The viscosity of apple purees (Dietini) decreased rapidly at low shear rate compared with apple puree (Odenwald). All of baby food products exhibited shear thinning

with yield stress behavior. Pear and banana in apple (HiPP) was more affected with shear rate than other type of baby food products, because the slope of shear stress was highest. In comparison of banana in apple products, product from Bebevita exhibited a similar viscosity of the one from HiPP, but the viscosity was decreased rapidly during shear test.

In Comparing rheological properties of the pineapple puree and the commercial products, rheological parameters matched the Ostwald-de Waele model, because the yield stress performed the same negative value as apple puree product, banana in apple puree (Bebivita) and pear puree (Bebivita). The flow index of pineapple puree (Final product) showed the lower value than commercial puree product. This can be described that the stability of pineapple product was better than commercial puree products. The viscosity of pineapple puree product exhibited the a little higher value than commercial puree products.

8.2.2 Oscillation test

The micro-structure of commercial puree products and pineapple puree (final product) were determined by using the oscillation test (frequency sweep and temperature sweep). Results were represented by oscillation parameter (G' (Storage modulus), G'' (loss modulus) and $\tan \delta$ (loss angular).

8.2.2.1 Frequency sweep

The frequency sweep was measured the structure of commercial product by using range of frequency from 0.01 to 10 Hz at temperature of 20 °C.

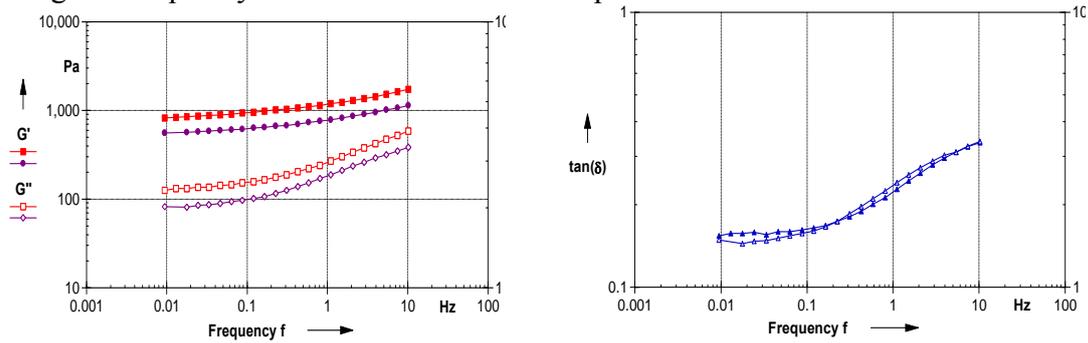


Figure 8.3 Oscillation parameters (temperature sweep) for two bands of apple puree products: dietini; G' (■), G'' (□), $\tan \delta$ (▲) and odenwald G' (●), G'' (○), $\tan \delta$ (Δ) at 20 °C

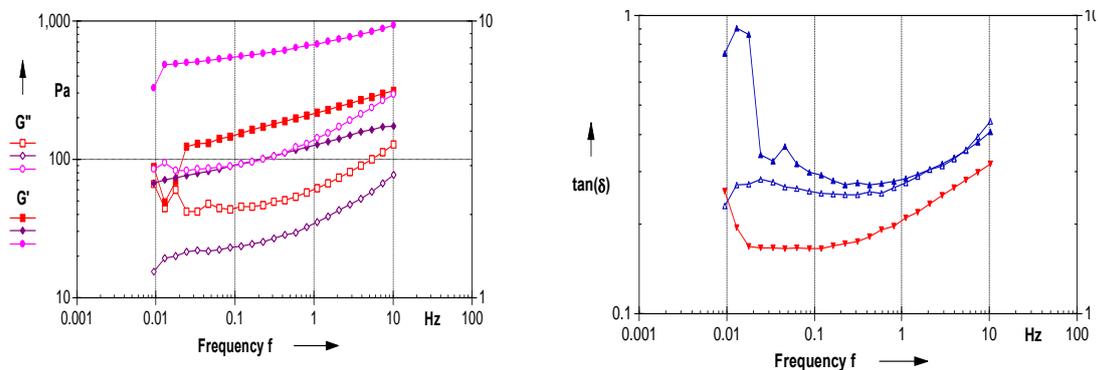


Figure 8.4 Oscillation parameters for three types of baby food products: banana in apple (bebevita); G' (■), G'' (□) and $\tan \delta$ (▲), and pear puree; G' (◆), G'' (◇), $\tan \delta$ (Δ) and banana in apple (HiPP); G' (●), G'' (○), and $\tan \delta$ (▼) at 20 °C

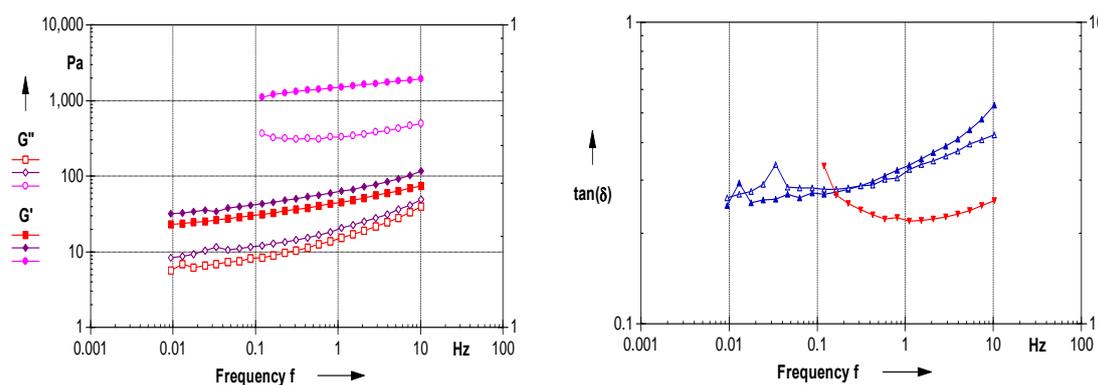


Figure 8.5 Oscillation parameters for three type of baby food products: peach in passion fruit; G' (■), G'' (□), $\tan \delta$ (▲) and peach in apple; G' (◆), G'' (◇), $\tan \delta$ (△) and fruit salad; G' (●), G'' (○), $\tan \delta$ (▼) at 20 °C

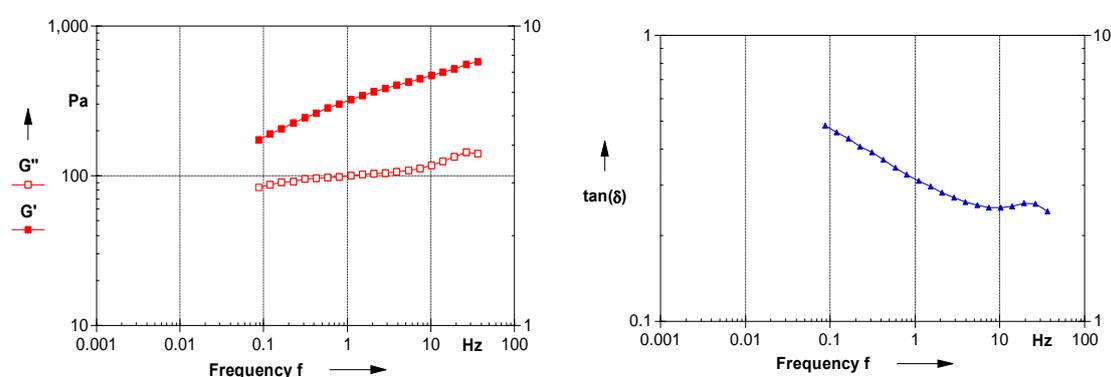


Figure 8.6 Oscillation parameters for pineapple puree added guar and xanthan gum

Results showed that all of samples performed that G' was higher than G'' at all range of frequency. This could be the reason that the puree product showed the particle gel behavior. Comparing the different bands of apple puree (Dietini and Odenwald) (Figure 8.3), both showed the similar value of parameter (G' , G'' and $\tan \delta$) value at all range of frequency. However, G' and G'' of apple puree (Dietani) were higher than apple puree (Odenwald), so the viscosity of apple puree (Dietani) was higher than other (Odenwald). A cross-over between G' and G'' did not occur in the tests, so the apple puree did not perform particle gel system According to figure 8.4, two bands of banana in apple puree product (Bebivita and HiPP) exhibited a significant gap between G' and G'' , particular gap of banana in apple (HiPP). It can be shown that banana in apple puree exhibited a viscoelasticity behavior and behaved more elastic behavior (Rao, 1999) compared with other baby food product in figure 8.5. The baby food products which contain the peach puree performed the narrow gap between G' and G'' . Thus, their behavior was less the elastic behavior compared with banana in apple puree. In the case of fruit salad sample, the low frequency (less than 0.1 Hz) could not be measured, because structure may be already destroyed. In the comparison with pineapple puree (final product), G' was increased with f and higher than G'' . However, $\tan \delta$ was decreased continually with f . Thus, pineapple puree exhibited more elastic behavior than commercial puree product.

8.2.2.2 Temperature sweeps

The temperature sweep investigated the effect of temperature range from 20 to 60 °C on the behavior of selected commercial puree products.

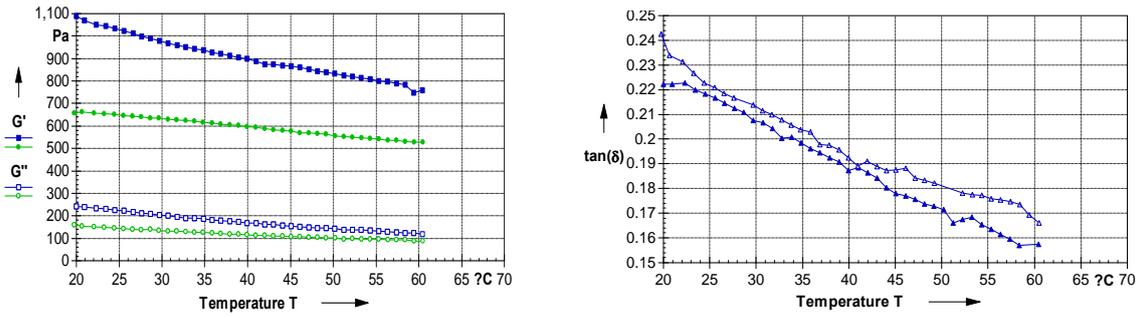


Figure 8.7 Oscillation parameters (temperature sweep) for two bands of apple puree products: dietini; G' (■), G'' (□), $\tan \delta$ (▲) and odenwald G' (●), G'' (○), $\tan \delta$ (Δ) at 20 °C

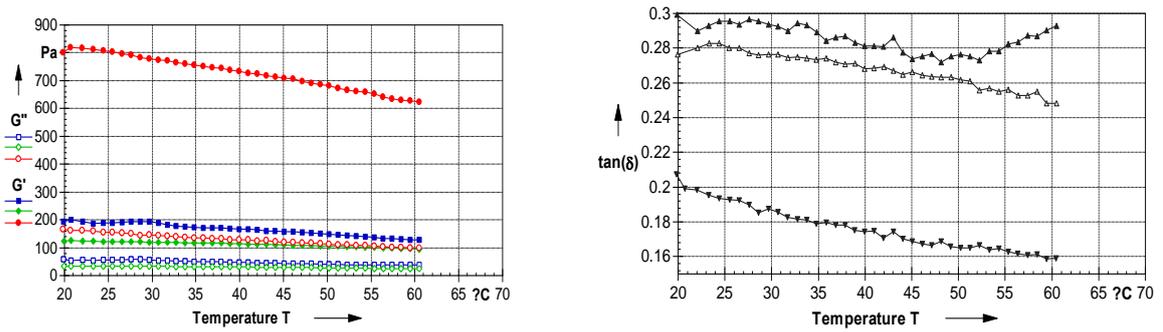


Figure 8.8 Oscillation parameters (temperature sweep) for three types of baby food products: banana in apple (Bebivita); G' (■), G'' (□), $\tan \delta$ (▲), pear puree; G' (◆), G'' (◇), $\tan \delta$ (Δ) and banana in apple (HiPP); G' (●), G'' (○), $\tan \delta$ (▼) at 20 °C

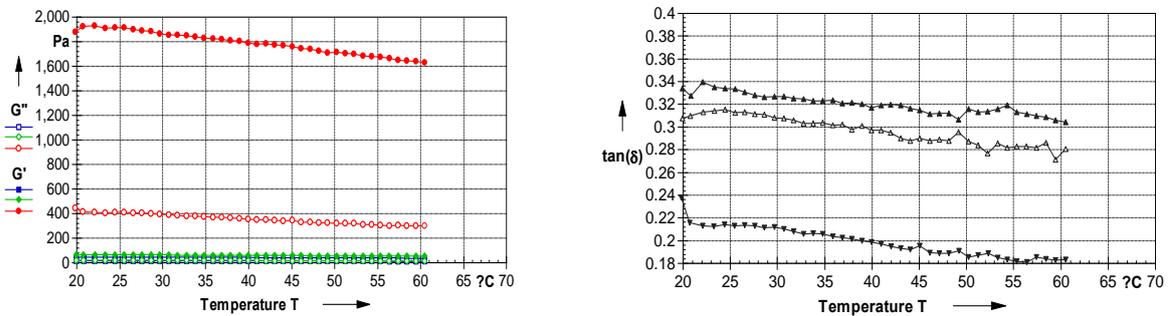


Figure 8.9 Oscillation parameters (temperature sweep) for three type of baby food products: peach in passion fruit; G' (■), G'' (□), $\tan \delta$ (▲), peach in apple; G' (◆), G'' (◇), $\tan \delta$ (Δ) and fruit salad; G' (●), G'' (○), and $\tan \delta$ (▼) at 20 °C

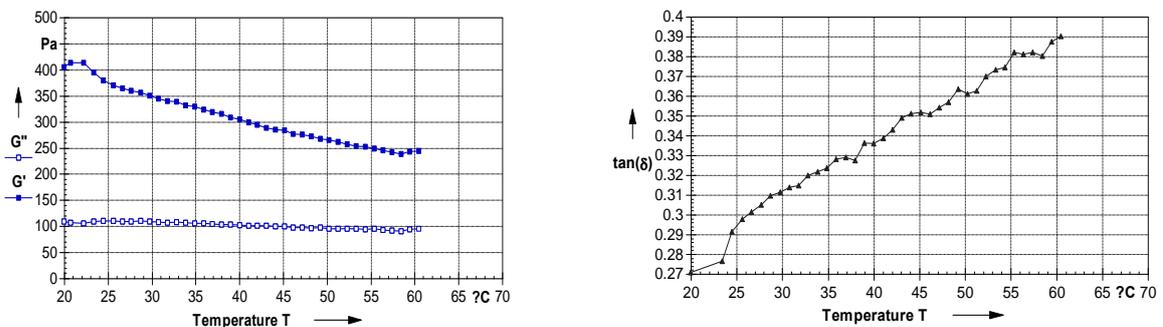


Figure 8.10 Oscillation parameters (temperature sweep) for pineapple puree (final product)

Results showed that all of samples performed that G' was higher than G'' at all range of temperature. There was no cross-over between G' and G'' . Thus, puree product performed viscoelasticity behavior and non-Newtonian with highly viscous fluid. The effect of temperature on the behavior of commercial puree products had little influence on the rheological behavior. It can see that G' and G'' decreased slightly. Comparing the two bands of apple puree (Bebivita, hipp) (Figure 8.7) showed a gap between G' and G'' apple puree (Dietini) was greater than apple puree (Odenwald) at all ranges of temperature. Thus, the apple puree (Dietini) showed more elastic behavior than apple puree (Odenwald). For baby food products results (Figure 8.8) showed the comparison between two bands of banana in apple puree (Bebivita and Hipp) and pear puree (Bebivita). The banana in apple from HiPP exhibited a significantly bigger gap than banana in apple (Bebivita) and pear puree, so banana in apple puree (HiPP) behaved more elastic behavior than other products. Fruit salad (Figure 8.9) showed the biggest gap in baby food products group. It can be described that fruit salad showed more elastic behavior than other baby food products. Figure 8.11 showed the decreasing rate of G' on temperature of 20 to 60 °C for pineapple puree and commercial puree products.

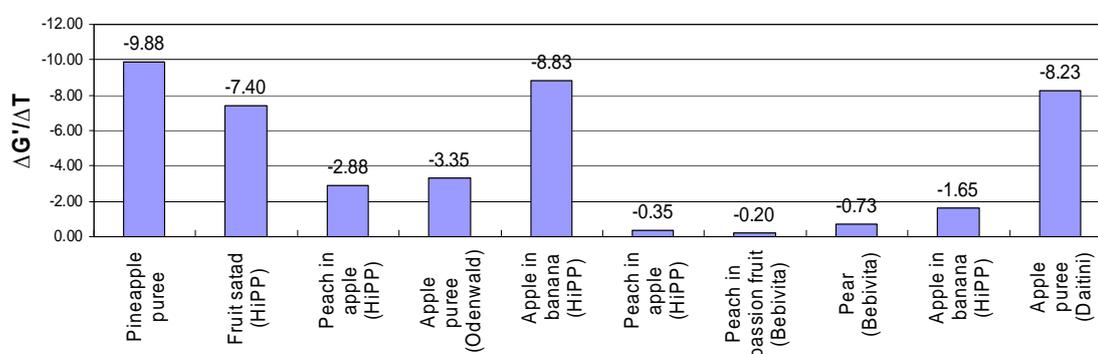


Figure 8.11 Decreasing rate of G' on temperature for pineapple puree and commercial puree products

In the Comparison with pineapple puree with commercial puree products, (Figure 8.10) G' and G'' was decreased slightly with increasing temperature the same as other product. However, $\tan \delta$ of pineapple puree was increased with temperature, but $\tan \delta$ of commercial products was decreased with temperature. Thus, pineapple puree exhibited more viscous behavior when temperature increased. It can be confirmed on figure 8.11, pineapple puree showed the lowest value of slope. Thus pineapple lost the elastic behavior when temperature increased. In contrast, the slope of G' on commercial product was higher than pineapple puree. Therefore, commercial puree products exhibited more elastic behavior when temperature increased.

8.3 Color examination of selected commercial products

The color examination of the products was carried out using parameters based on three color co-ordinates, namely L a b. Results showed that the color of puree (Figure 8.12) was depended on the type of fruit in puree. In the L parameter (Lightness), all of samples showed similar results range from 40.82 to 53.69. The results of a parameter (red color), showed that apple puree from Odenwald showed had the lowest and negative value. Therefore, apple puree (Odenwald) appeared the green color compared with the other product, which showed more red color appearance.. The b parameter results showed that apple puree (Odenwald), banana in apple (Bebivita) and Pear (Bebivita) had a low value, but were still the positive value. Thus, the color of three of them appeared light yellow color. In comparing pineapple puree and other commercial puree products, lightness of pineapple

puree showed no difference from the other products. Pineapple puree showed the yellow color less than other product. In contrast, pineapple puree appeared more green color than commercial puree products, except apple puree from Odenwald. In the conclusion, puree products appeared in yellow appearance.

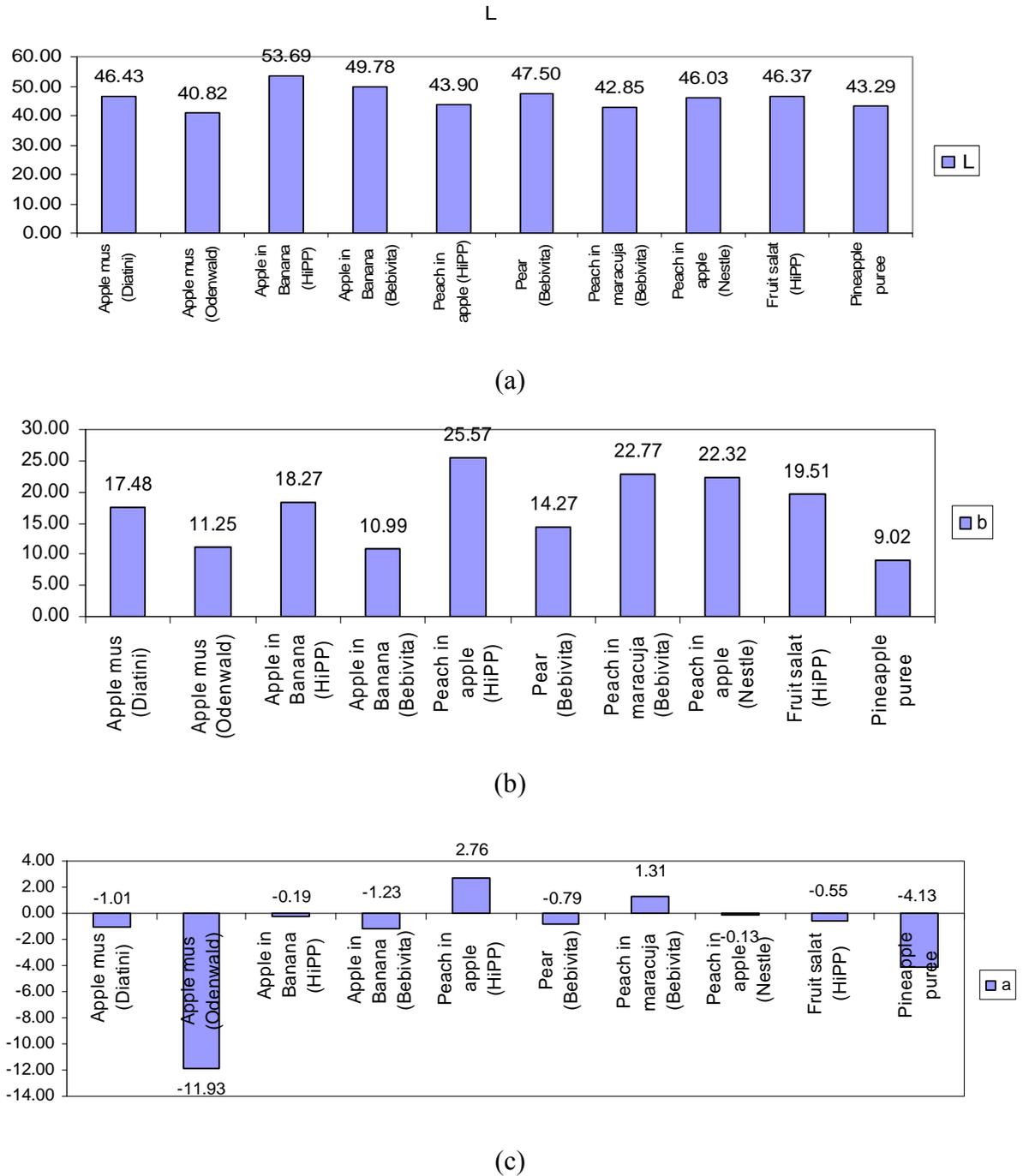


Figure 8.12 Color parameter for selected commercial products; L (a), a (b) and b (c)

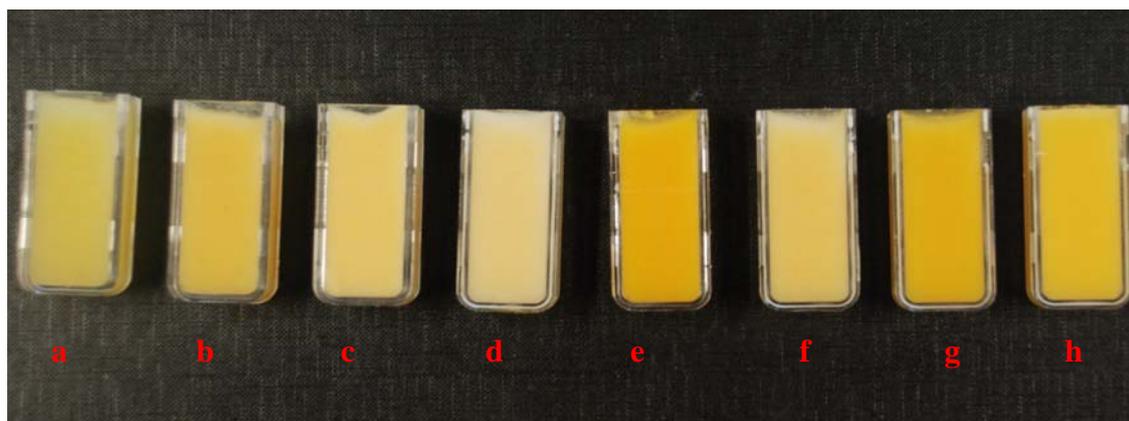


Figure 8.13 Color of selected commercial products: apple puree (odenwald) (a), apple puree (dietini) (b), banana in apple (HiPP) (c), banana in apple (bebivita) (d), peach in apple (HiPP) (e), pear (bebivita) (f), peach in passion fruit (g) and fruit salad (HiPP) (h)

In the conclusion, comparing pineapple puree and commercial puree products, the color properties of pineapple puree showed less yellow color and darker than commercial products. In the case of physicochemical properties, Total soluble solid and pH showed the similar result as commercial products. For the rheological properties, the stability and viscosity of pineapple puree was better than commercial puree products. Therefore, pineapple puree (final product) can be considered to have better characteristics than commercial puree products. However, pineapple puree products need to be tested by consumers.

Chapter 9 Further studies recommendation

Investigate another advance type of stabilizer for stabilizing structure of pineapple puree, such as xyloglucan.

Pineapple contains some of pectin. Pectin from pineapple will be investigated the method of extraction. The advantage of pectin on pineapple product was that the flavor and taste of pineapple will be not interfered by flavor of gum. Furthermore, the flavor of pineapple will enhance by gum as well.

Study another preparation of pineapple puree, such as high pressure extraction or use vacuum extraction for making concentration pineapple puree, on rheological properties.

Study the consumer acceptance of pineapple puree product by using sensory evaluation method with trained panel and untrained panel.

Study possibility to apply gums pineapple puree industries. Furthermore, investigate flow behavior on in-line production was also importance in bakery industries.

Study rheological properties of another fruit puree, such as mango, banana or orange. The composition of orange is similar to pineapple, so orange has the possibility to behave the rheological same as pineapple after making puree. Therefore, application of stabilizer is able to add in orange puree.

Study the rheological properties of fruit mixture, such as apple and pineapple puree mixture, papaya and pineapple mixture. Gums are used to control rheological properties, such as stability and viscosity.

Chapter 10 Conclusion

Aim of this study was to investigate the raw material and method of pineapple puree. The raw material studied the characteristic of fresh pineapple fruit during storage time. That was included to classify the maturity state of pineapple fruit. The method of pineapple puree investigated to improve the rheological properties by using the stabilizers, such as pectin, guar, LBG, xanthan gum.

In order to stabilize structure of pineapple puree by using gums, the stability and viscosity of pineapple puree showed best value, when added the mixed gum between guar gum and xanthan gum at ratio 75:25. In contrast, pineapple puree added single gums showed the good stability, when added xanthan gum of 1 %.

To determine the characteristic of pineapple fruits on different level of maturity: the quality of pineapple was depended on the level of maturity, such as color, texture, pH changing. Color of skin was changed from green to yellow. Color of pulp was dark. Texture of pineapple pulp was became soft and less firmness with increasing level of maturity

Influence of Ca-ion, DE and concentration on pectin solution showed that the Ca-ion has significantly effect with low DE pectin more than High- and amidate-pectin. Ca-ion has effect with Low-DE pectin than other pectins. The influence of DE showed that high-DE of pectin performed the good stability, but viscosity was not high. In contrast, the amidate pectin showed the good stability and viscosity.

Influence of concentration of LBG on rheological properties, the stability and viscosity of LBG was increased with concentration. Temperature has the effect with high of LBG than low concentration. The rheological properties of guar gum solution performed the same as LBG solution. Xanthan gum solution showed the same rheological properties as LBG and guar gum, but it exhibited the yield point. The temperature didn't have effect with xanthan gum significantly.

Synergistic between LBG and xanthan performed stronger interaction than a combination between guar and xanthan gum. It can be seen that the viscosity of combination between LBG and xanthan gum higher than another combination

Effect of type of pectin, concentration of pectin and sugar content on pineapple puree showed that pineapple puree added amidated citrus pectin performed the good viscosity and stability. Effect of sugar content in pectin showed sugar particle was interfere the structure of pineapple puree and pectin, consequently, the stability of pineapple puree was reduced with added sugar. Stability of pineapple puree was increased with concentration of pectin.

Effect of LBG in pineapple puree showed that stability of pineapple puree was decreased with increased concentration. Pineapple puree added 0.2 to 0.8 % of LBG decreased stability rapidly. Stability of pineapple puree was not changed after added LBG more than 1 %. The temperature has the effect with high concentration of LBG more than low concentration. Pineapple puree with guar gum showed increased viscosity and stability with concentration. Temperature has effect with guar gum the same as pineapple with LBG. The stability of pineapple puree with xanthan gum performed increased with concentration, but viscosity was increased with small among of value. Temperature has no a lot of effect with pineapple added xanthan gum.

The synergistic of galactomannan and xanthan gum in pineapple puree showed that combination of guar gum and xanthan gum performed can improved the stability better than LBG and xanthan gum. Mixed gum can improved the stability and viscosity compare with single gum, such as xanthan gum, locust bean and guar gum.

To compare between pineapple puree and commercial puree products, pineapple puree at best stabilizer (mixed gum) exhibited higher stability and viscosity than commercial puree. The pH and total soluble solid of pineapple puree showed no difference with commercial puree. Pineapple puree showed lighter yellow than commercial puree products.

In the conclusion, the stabilizers had the potential to use bakery industries or pineapple puree canned products. The pineapple puree could use the stabilizer to retain the stability during storage or transportation. Furthermore, the stabilizers control the flow properties of pineapple puree in production process. The controlled flow properties of pineapple puree in process is able to the save energy in process.

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Chapter 12. Appendix

APPENDIX A: Oscillation test

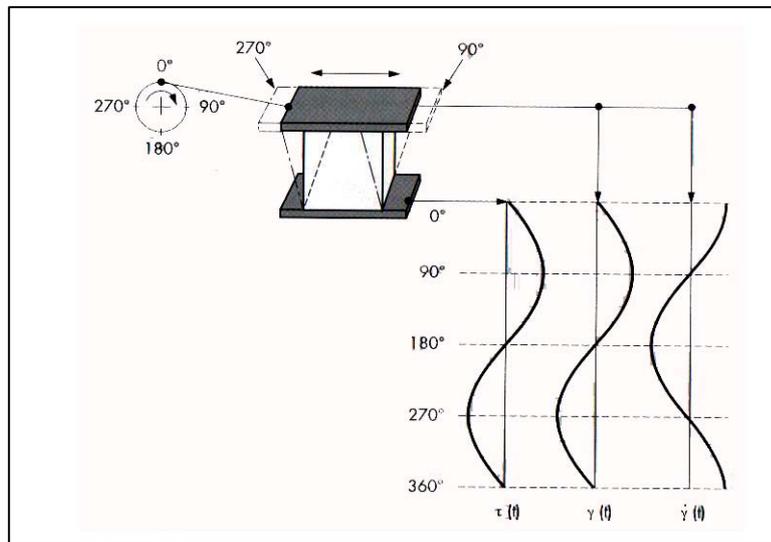


Fig. A-1 Oscillation behavior for ideal elastic component (Mezger, 2006)

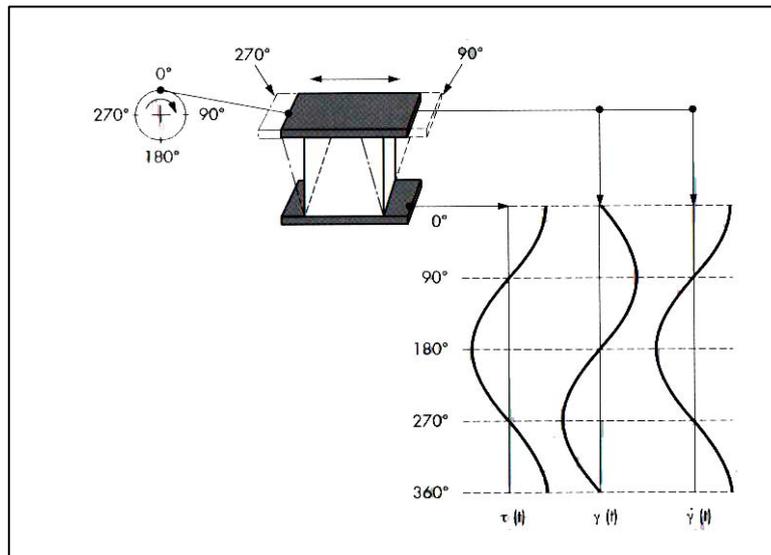


Fig. A-2 Oscillation behavior for ideal viscous component (Mezger, 2006)

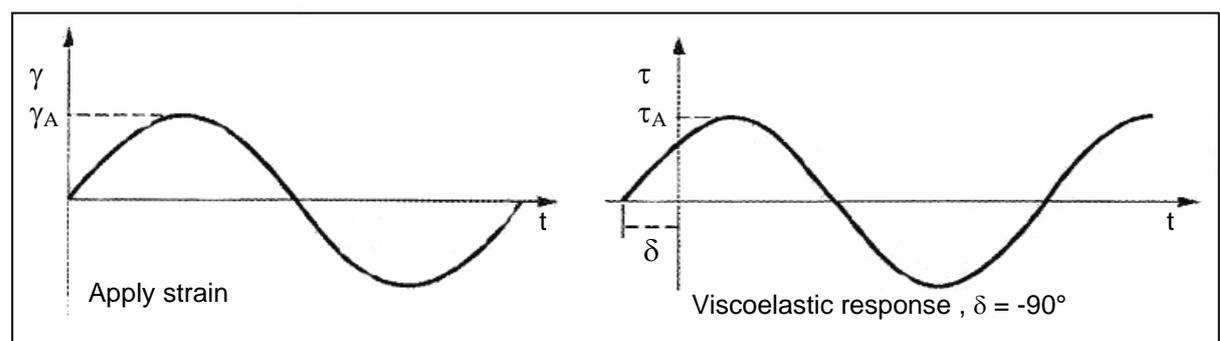


Fig. A-3 Oscillation behavior for viscoelastic component (Mezger, 2006)

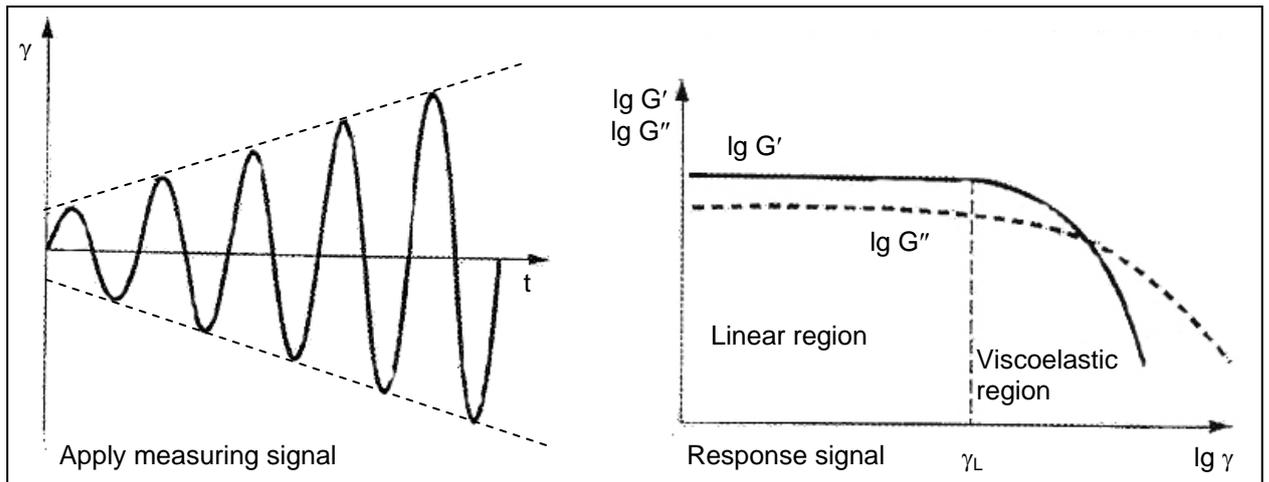


Fig. A-4 Amplitude sweep test (Mezger, 2006)

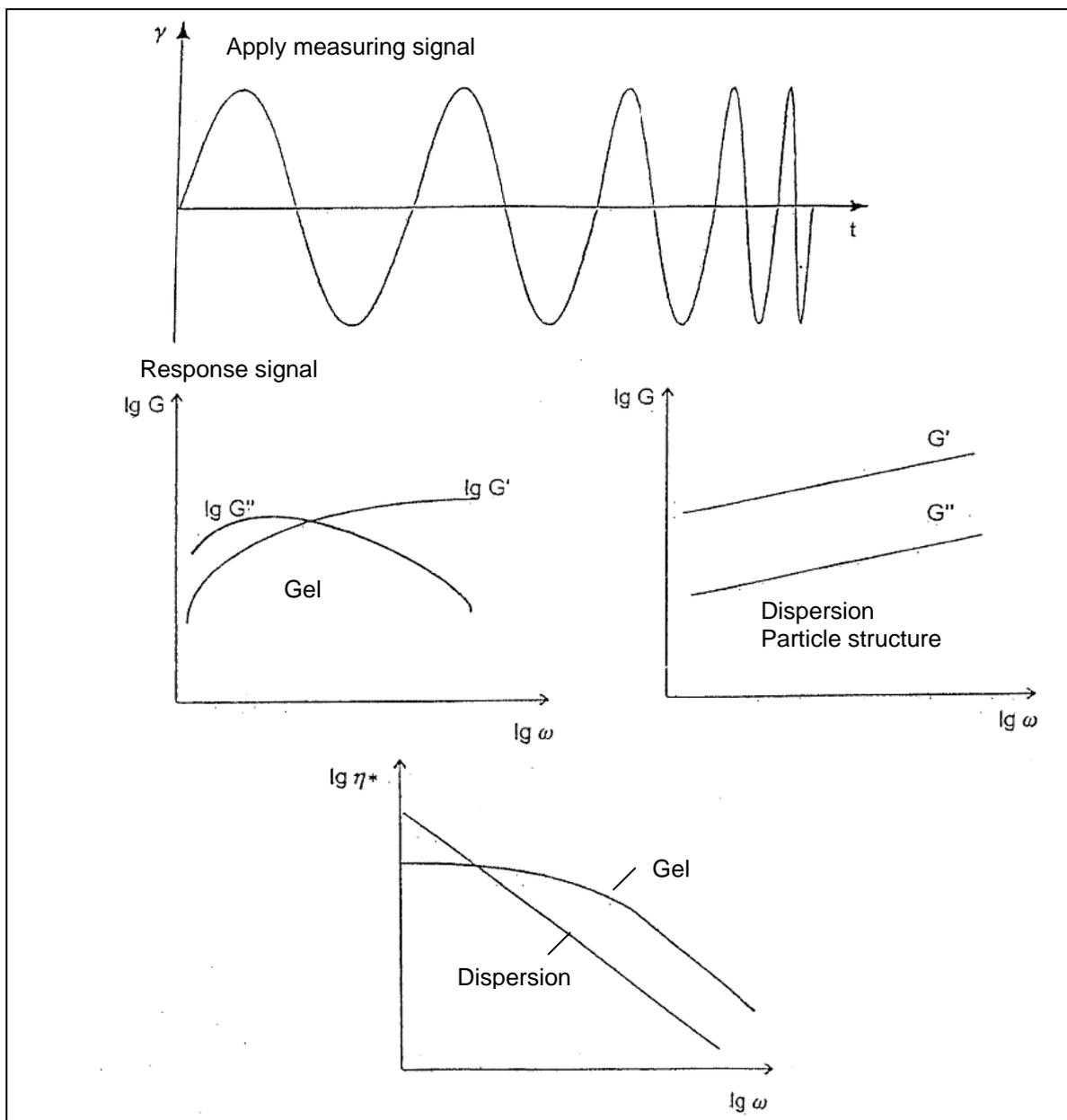


Fig. A-5 Frequency sweep test (Mezger, 2006)